

BEST AVAILABLE COPY

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

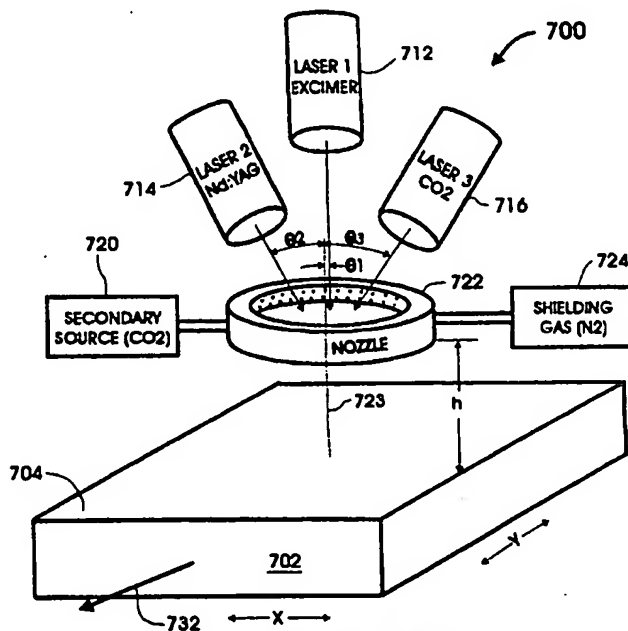
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : H01S		(11) International Publication Number: WO 95/20253
A2		(43) International Publication Date: 27 July 1995 (27.07.95)
(21) International Application Number: PCT/US95/00782		(US). TURCHAN, Manuel [US/US]; 42288 Crestview, Northville, MI 48167 (US).
(22) International Filing Date: 17 January 1995 (17.01.95)		(74) Agent: LINDEN, Gerald; 2716 S. Chickasaw Tr., Orlando, FL 32829 (US).
(30) Priority Data: 08/182,978 18 January 1994 (18.01.94) US 08/184,041 21 January 1994 (21.01.94) US 08/241,930 12 May 1994 (12.05.94) US		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ).
(60) Parent Applications or Grants (63) Related by Continuation US 08/241,930 (CIP) Filed on 12 May 1994 (12.05.94) US 08/184,041 (CIP) Filed on 21 January 1994 (21.01.94) US 08/182,978 (CIP) Filed on 18 January 1994 (18.01.94)		Published Without international search report and to be republished upon receipt of that report.
(71) Applicant (for all designated States except US): QQC, INC. [US/US]; 12825 Ford Road, Dearborn, MI 48126 (US).		
(72) Inventors; and (75) Inventors/Applicants (for US only): MISTRY, Pravin [GB/US]; 3410 24 Mile Road, Shelby Township, MI 48136		

(54) Title: USING LASERS TO FABRICATE DIAMOND, DIAMOND-LIKE CARBON, AND OTHER MATERIAL COATINGS ON SUBSTRATES

(57) Abstract

Laser energy is directed at a substrate to mobilize, vaporize and react a constituent (primary) element (e.g., carbon) contained within the substrate, so as to modify the composition (e.g., crystalline structure) of the constituent element, and to diffuse the modified constituent back into the substrate, as an adjunct to fabricating a coating (e.g., diamond or diamond-like carbon) on the surface of the substrate. This creates a conversion zone immediately beneath the substrate, which transitions metallurgically from the composition of the underlying substrate to a composition of the coating being fabricated on the surface of the substrate, which results in diffusion bonding of the coating to the substrate. Additional (secondary) similar (e.g., carbon) or dissimilar elements may be introduced in a reaction zone on and above the surface of the substrate to augment the fabrication of and to determine the composition of the coating. The laser energy is provided by a combination of an excimer laser, and Nd: YAG laser and a CO₂ laser, the output beams of which are preferably directed through a nozzle delivering the secondary element to the reaction zone. The reaction zone is shielded by an inert (non-reactive) shielding gas (e.g., N₂) delivered through the nozzle. A flat plasma is created by the lasers, constituent element and secondary element on the surface of the substrate and the flat plasma optionally extends around the edges of the substrate to fabricate a coating thereon. Pre-treatment and coating fabrication can be performed in conjunction with one another (in-situ). Alternatively, a substrate can be pre-treated to characterize its surface for subsequent coating. In either case, certain advantageous metallurgical changes are induced in the substrate due to the pre-treatment. The processes (pre-treatment and coating fabrication) are suitably performed in ambient, without preheating the substrate and without a vacuum. Substrates of numerous geometries, sizes and shapes, such as flat cutting tool inserts as well as round cutting tools, are readily coated in this manner. The lasers are directed at any suitable angle (including coaxial) relative to the substrate and/or the plasma.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

WO 95/20253

PCT/US95/00782

TITLE

USING LASERS TO FABRICATE DIAMOND, DIAMOND-LIKE
CARBON, AND OTHER MATERIAL COATINGS ON SUBSTRATES

CROSS-REFERENCE TO RELATED APPLICATIONS

5 This application is a continuation-in-part of commonly-
owned, copending U.S. Patent Application No. 08/241,930, filed
May 12, 1994 by Mistry and Turchan ("PARENT-III"; status:
pending).

10 This application is a continuation-in-part of commonly-
owned, copending U.S. Patent Application No. 08/184,041, filed
January 21, 1994 by Mistry and Turchan ("PARENT-II"; status:
pending).

15 This application is a continuation-in-part of commonly-
owned, copending U.S. Patent Application No. 08/182,978, filed
January 18, 1994 by Turchan and Mistry ("PARENT-I"; status:
pending).

WO 95/20253

PCT/US95/00782

TECHNICAL FIELD OF THE INVENTION

The present invention relates to the surface treatment of substrates, for example metal substrates, the surface treatment including fabricating materials such as diamond and diamond-like carbon on the surface of the substrate.

BACKGROUND OF THE INVENTION

The present invention relates to the fabrication of coatings such as diamond, diamond-like carbon (DLC), Cubic Boron Nitride (CBN), B_4C , SiC , TiC , Cr_3C_2 , TiN , TiB_2 , Si_3N_4 and cCN , on substrates. In the main hereinafter, the fabrication of a diamond coating on a tungsten carbide cutting tool insert (substrate) is discussed, but the invention is not limited thereto.

It is generally well known that coating a substrate, such as applying a diamond or diamond-like carbon (DLC) coating to a substrate, can enhance the substrate's properties. For example, a diamond (or DLC) coated cutting tool insert will generally facilitate greater tool speed, feed rate and depth of cut, will generally exhibit longer tool life, will result in a superior finish on the workpiece, and will facilitate dry (no lubrication required) machining of workpieces. Round tools such as drills and end mills will exhibit similar advantages when coated with diamond (or DLC).

CVD DEPOSITION PROCESSES

There are a number of chemical vapor deposition (CVD) deposition processes currently in use, for depositing diamond coatings. Generally, these processes involve the dissociation and ionization of hydrogen and methane precursor gases, which are then passed over and deposited (e.g., precipitated) onto a

WO 95/20253

PCT/US95/00782

heated substrate. Generally, these processes involve the use of plasma, microwave, hot filament, ion beam, and electron beam as energy sources, and the use of a mixture of 0.5% to 2.0% methane and the balance hydrogen gas as a carbon source (precursor gas). Generally, processes which employ one or another form of CVD are inherently limited in that they require the use of a vacuum chamber (thereby complicating the process and limiting the size of the substrate that can be coated) and involve significant controlled heating and subsequent cooling of the substrate. (thereby limiting its efficacy to certain types of substrates). The need to heat the substrate in order to apply the coatings is, in many ways, counterproductive. Such application of heat to the entire substrate (mass heating of the substrate) can cause distortion of the substrate, and the loss of any temper (heat treatment) that had previously been present in the substrate. For example, in the heated filament CVD method, a tungsten or tantalum filament is used to heat the precursor gases to about 2000°C. Substrate temperature ranges from 600-1100°C. Another disadvantage of CVD processes is that the cycle time is generally on the order of hours, for coating a limited number of parts. Generally, deposition rates are low, on the order of 1-10µm per hour (using hydrogen and methane precursors). Other deposition processes, similar to CVD, are similarly limited.

In DC plasma CVD, a DC (direct current) arc is used to dissociate the precursor gases, and can provide higher gas volumes and velocities than other prior art processes.

Microwave (or microwave-plasma enhanced) CVD uses microwaves to excite the precursor gases, resulting in deposition rates of several microns per hour. Coatings deposited using this method tend to be of very high purity.

Another coating process, closely related to CVD, is

WO 95/20253

PCT/US95/00782

Physical Vapor Deposition (PVD). In PVD, a target in a vacuum chamber is evaporated, as opposed to introducing a gas to the vacuum chamber with CVD.

In CVD and PVD (e.g., deposition-type) processes:

- 5 • there is a need to significantly elevate the temperature of the substrate. (Note that high temperatures are not necessary in PVD to produce DLC-type coatings.)
- there is a significant (2-5 hour) cooling time, during which time residual precursors (gas or evaporated target
- 10 materials) deposit, like snowflakes, on the surface being coated. This results in a coating which has a very rough surface, as compared to the pre-coated surface, and which typically requires post-processing to achieve a smoother surface.
- 15 • when depositing a diamond (or DLC) coating, an amorphous coating is typically formed, containing either SP^2 -bonded carbon or SP^2 -bonded carbon and SP^3 -bonded carbon, with higher concentration of hydrogen.
- both CVD and PVD processes are directed to depositing a
- 20 material on the surface of a substrate, and rely on molecular bonding, and typically on some mechanical keying.
- PVD coatings tend to be porous. CVD coatings tend to be somewhat less porous than PVD coatings.
- both CVD and PVD processes are generally limited in
- 25 suitability to coating flat surfaces, or simple (non-complex geometry) round surfaces.
- the size of the substrate that can be coated is limited by the size of the vacuum chamber in which the process is carried out; the size of the substrate is typically less than
- 30 eight inches in diameter.
- inasmuch as these processes tend to rely primarily on a precipitation-type (i.e., generally directional deposition) mechanism, the "other" side of the substrate may exhibit shadowing or uneven deposition.

WO 95/20253

PCT/US95/00782

• CVD processes may also require substrate preparation (prior to coating), including surface chemistry modification, seeding, and the like.

USP 5,308,661 ("FENG"; 5/94; 427/535), entitled
5 PRETREATMENT PROCESS FOR FORMING A SMOOTH SURFACE DIAMOND FILM
ON A CARBON-COATED SUBSTRATE, incorporated by reference herein,
is indicative of CVD processes, and discloses applying a carbon-
containing coating to the surface of a substrate, said carbon-
containing coating having a concentration and thickness
10 sufficient to provide a uniform density or concentration of
carbon atoms in the resultant coating on the substrate surface
of at least 10 atoms/ μm^2 . The carbon-coated substrate is then
exposed to a microwave plasma in a vacuum chamber, in a
microwave-plasma enhanced chemical vapor deposition (MECVD)
15 system. Methane and hydrogen gas is introduced into the system.
After these pre-treatment steps, a diamond layer is grown on the
coated substrate, using conventional processing, such as MECVD
at a higher pressure (than the pre-treatment) and with reduced
methane flow (ratio of methane to hydrogen 0.15% - 4.0% methane,
20 preferably from 0.5% -1.0% methane). FENG differs from the
present invention, inter alia, in that the surface treatment
technique of the present invention does not require first
coating the substrate with a carbon-containing coating, the
surface treatment technique of the present invention does not
25 require a CVD process, and the surface treatment technique of
the present invention advantageously employs laser energy to
fabricate a coating on a substrate. FENG does, however, suggest
that the "conventional" (i.e, accepted) method of applying a
diamond coating to a substrate is to use a CVD process.

30 COBALT POISONING

A problem which manifests itself in coating processes generally, and particularly in CVD (and related) processes, is

WO 95/20253

PCT/US95/00782

evident when forming a diamond (or DLC) coating on a tungsten carbide substrate. Carbide (tungsten carbide grains in a cobalt binder) has long been an established choice for use in cutting tools and inserts, especially for cutting (machining) ferrous, nonferrous or abrasive materials such as aluminum and its alloys, copper, brass, bronze, plastics, ceramics, titanium, fiber-reinforced composites and graphite. Various forms of carbide are known for tools and inserts, such as cobalt-consolidated tungsten carbide (WC/Co). The presence of cobalt in the substrate, tends to present a problem when seeking to apply a diamond coating to a tool insert. The cobalt binder phase found in carbide tools essentially "poisons" the diamond nucleation and growth process, resulting in formation of graphitic carbon rather than diamond (or DLC).

WO 95/20253

PCT/US95/00782

LASER-ASSISTED COATING PROCESSES

Recently, it has become known to use energy supplied from a laser in conjunction with forming a diamond coating or film on a substrate. A number of techniques employing laser energy are discussed below as exemplary of such techniques, and are incorporated by reference herein for the purpose of providing background information. The citation format is "USP" (indicating US Patent Number), followed by ("FIRST NAMED INVENTOR"; date of issue; class/subclass), all of which are underlined.

USP 5,154,945 ("BALDWIN"; 10/92; 427/596) discloses two techniques of depositing diamond thin films onto a substrate. In one embodiment ("BALDWIN-I"), the deposition of the film is from a gas mixture of CH₄ (methane) and H₂ (hydrogen) that is introduced into a CVD chamber and caused to flow over the surface of the substrate to be coated while a laser is directed onto the surface. This embodiment generally suffers from all of the inherent limitations of conventional CVD processes. In another embodiment ("BALDWIN-II"), pure carbon in the form of soot is delivered onto the surface to be coated, and the laser beam is directed onto the surface in an atmosphere that prevents the carbon from being burned to CO₂. In BALDWIN-II, a CO₂ gas laser beam is directed at normal incidence onto the surface to be coated. Movement between the substrate and the laser beam causes momentary heating of a very small area of the substrate surface with minimum energy input, resulting in a diamond deposit on the surface with almost no disturbance of the substrate.

The "conventional wisdom" of not affecting the substrate while applying laser energy is also set forth in USP 5,273,788 ("YU"; 12/93; 427/554), entitled PREPARATION OF DIAMONDS AND DIAMOND-LIKE THIN FILMS, which discloses applying a layer of a

WO 95/20253

PCT/US95/00782

hydrocarbon molecule to a substrate by the Langmuir-Blodgett technique, and irradiating the surface with a laser to decompose the layer of molecules at the surface without influencing the substrate.

5 USP 4,981,717 ("THALER"; 1/1/91; 427/53.1), entitled
DIAMOND LIKE COATING AND METHOD OF FORMING, discloses a method
of depositing diamond-like films from a plasma of a hydrocarbon
gas precursor. The plasma is generated by a laser pulse which
is fired into the gas and is absorbed in an "initiator" mixed
10 with the gas. The resulting detonation produces a plasma of
ions, radicals, molecular fragments and electrons which is
propelled by the detonation pressure wave to a substrate and
deposited thereon. This, and any technique like it, is
analogous to rain (diamond particles) falling on a pond (the
15 substrate being coated), and tends to result in a coating which
is not adhered well to the substrate and which requires post-
finishing to achieve a desired surface finish on the coated
substrate.

THALER discusses the use of precursor gases such as a
20 hydrocarbon, for example methane, ethane, propane, ethylene,
acetylene, or similar hydrocarbon gases and vapors. This gas
is cracked by intense heat to form a variety of high energy
fragments, ions, radicals and free electrons. Cracking is
achieved by subjecting the hydrocarbon to intense laser pulses,
25 for example, CO₂ laser having a 50 nanosecond spike and a power
output of 10¹⁴ watts/cm².

THALER discusses the user of an "initiator" which is mixed
with the hydrocarbon gas or vapor. The initiator is preferably
a compound which is strongly absorbing at the output wavelength
30 of the laser impulse used. The output wavelength for a CO₂
laser is 10.6 microns (μm), and sulfur hexafluoride (SF₆) is a
highly effective initiator when used with such a laser,

WO 95/20253

PCT/US95/00782

providing both sulfur and fluoride ions and radicals upon detonation. The initiator serves to accumulate the applied (laser pulse) energy, in a very small volume, releasing same explosively, fragmenting the hydrocarbon into highly reactive ions and radicals, and imparting high translational energy to the formed gases. The coating resulting from these detonations will have properties of both diamond and fluorocarbons.

USP 4,948,629 ("HACKER"; 8/90; 427/53.1), entitled DEPOSITION OF DIAMOND FILMS, discloses depositing diamond films on substrates below temperatures of 400°C, and preferably less than 150°C, by chemical vapor deposition using a high powered pulsed laser and a vapor which is an aliphatic carboxylic acid or an aromatic carboxylic anhydride. The process requires the use of a high powered, pulsed laser, such as an excimer laser or a Nd:YAG laser. Preferred excimer laser wavelengths include KrCl at 220nm, KrF at 248 nm, XeCl at 308 nm, and XeF at 351nm. Preferred Nd:YAG wavelengths include the fourth harmonic at 266 nm and the third harmonic at 355 nm.

HACKER discusses using a second laser of longer wavelength (>400 nm), e.g., a second harmonic of Nd:YAG at 532nm, to selectively remove sp² carbon and deposit a purer diamond film. An example is given whereby the diamond deposition was initiated by a 248nm laser beam (KrF excimer laser) photodissociation of the organic precursor (malonic acid or pyromellitic dianhydride, with helium added as a buffer gas), followed by using a 532nm laser beam (second harmonic Nd:YAG) to photo-ablate any non-diamond inclusions in the film. By virtue of using lasers to augment a CVD process, HACKER is subject to the aforementioned limitations (e.g., significant preheating of the substrate, limited substrate sizes) which are inherent to CVD processes.

USP 4,954,365 ("NEIFIELD"; 9/90; 427/53.1, entitled METHOD OF PREPARING A THIN DIAMOND FILM, discloses preparing a thin

WO 95/20253

PCT/US95/00782

diamond film by immersing a substrate in a liquid containing carbon and hydrogen, and then subjecting the substrate to at least one laser pulse. For example, a silicon substrate is immersed in methanol, in a vessel having a quartz window through which laser light may be introduced. An excimer laser pulse, with a wavelength of 248 nm and a pulse duration of about 20 nanoseconds is intercepted by the silicon substrate. The substrate absorbs the laser light and becomes heated. The methanol in contact with the heated substrate is pyrolyzed. Carbon material from the pyrolyzed methanol then grows on the substrate, and the high density of hydrogen reacts with and removes from the substrate any carbon which does not have diamond bonds. Repeated application of the laser pulse continues growth of the diamond film on the substrate. NEIFIELD requires a substrate that is absorptive of laser light, such as the aforementioned silicon substrate.

USP 5,290,368 ("GAVIGAN"; 3/94; 148/212), entitled PROCESS FOR PRODUCING CRACK-FREE NITRIDE-HARDENED SURFACE ON TITANIUM BY LASER BEAMS, discloses preheating a titanium substrate (using a furnace to elevate the temperature of the substrate to between 1000 and 1200 degrees Fahrenheit), melting a small area of the substrate with a laser (such as a 5 kW, CO₂, continuous wave laser, operating in the power range of 3.1 Kw to 3.6 kW), and shrouding the melted area with a gas mixture (containing, by volume, at least 70% but not more than 85% nitrogen, the balance being one or more gases that do not react with molten titanium). GAVIGAN discusses the use of other lasers, including a continuous wave YAG laser, and a pulsed CO₂, YAG or excimer laser. Generally, as the laser scans over the surface of the substrate the melted area not (no longer) under the laser beam is rapidly solidified due to the heat absorption of the unmelted substrate. GAVIGAN discusses that the process will work with other alloys of titanium that contain other strong nitride formers in their composition, such as vanadium, columbium,

WO 95/20253

PCT/US95/00782

carbon and aluminum. Although not directed to forming a coating, per se, GAVIGAN is gratuitously cited herein, without prejudice, as representative of performing other processes (i.e., than forming coatings), on other (i.e., other than steel) materials, with lasers, although its teachings would appear to be limited to producing a crack-free nitride-hardened surface on titanium and its alloys.

USP 5,236,545 ("PRYOR"; 8/93; 156/613), which discloses a process involving the deposition of a cubic boron nitride (CBN) layer on a silicon substrate as a first interfacial layer using laser ablation with a hexagonal boron nitride target in a nitrogen-containing atmosphere., followed by a second interfacial layer of hydrogen terminated carbon which is deposited with laser ablation with a carbon target in the presence of atomic hydrogen, followed by deposition of a heteroepitaxial diamond film using conventional chemical vapor deposition (CVD) technique.

USP 5,098,737 ("COLLINS"; 3/92; 427/53.1) discloses directing a laser beam at a target at non-perpendicular angles of incidence. This patent provides a useful background on the four major methods being investigated for producing diamond-like carbon films: (1) ion beam deposition, (2) chemical vapor deposition, (3) plasma enhanced chemical vapor deposition, and (4) sputter deposition. Broadly speaking, this patent discloses a laser directed within a vacuum chamber to impinge upon a continuous sheet of moving target material made of graphite foil placed within the chamber. The laser beam is focused upon the target material to ablate and to eject a plume of carbon vapor, whereby the plume is partially ionized by the laser beam.

USP 5,094,915 ("SUBRAMANIAM"; 3/92; 428/408), entitled LASER-EXCITED SYNTHESIS OF CARBON FILMS FROM CARBON MONOXIDE-CONTAINING GAS MIXTURES, discloses a method for forming a carbon

WO 95/20253

PCT/US95/00782

film on a substrate by irradiating a carbon monoxide containing gas with an emission from carbon monoxide laser without irradiating the substrate with the laser emission.

5 USP 5,080,752 ("KABACOFF"; 1/92; 156/603) discloses a
process in which particles of transparent diamond powders are
bonded together by polycrystalline diamond to form useful
diamond structures. An intimate mixture of fine opaque
nondiamond carbon powder and transparent diamond powder is
pressed together to form a green body that is confined in either
10 a thin walled transparent quartz vessel or a polycrystalline
diamond coating, and a pulse laser is used to quickly melt the
opaque nondiamond carbon powder. Then, the carbon melt is
allowed to cool and grow homoepitaxially from the surfaces of
the diamond particles, producing a polycrystalline diamond that
15 bonds the diamond particles together.

USP 5,066,515 ("OHSAWA"; 11/91; 427/53.1) discloses a
method of forming an artificial diamond comprising applying a
laser beam to a glassy solid carbon material while moving a
point on the glassy solid carbon material at which the laser
20 beam is applied, to form a locally fused portion thereon,
whereby every part of the locally fused portion is cooled as the
point moves away therefrom. During cooling of the locally fused
portion, an artificial diamond is formed in adjacent regions on
both sides of the solidified locally fused portion;

25 USP 4,987,007 ("WAGAL"; 1/91; 427/53.1) discloses producing
a layer of material on a substrate by extracting ions from a
laser ablation plume in a vacuum environment. The apparatus
includes a vacuum chamber containing a target material and a
laser focused on the target to ablate the material and ionize
30 a portion of the ablation plume, and is suitable for forming
diamond-like carbon films on a clean, unseeded silicone
substrate. The process can produce a DLC layer of exhibiting

WO 95/20253

PCT/US95/00782

uniform thickness with less than 3% variation at a rate of 20 μm per hour. The process involves focusing a laser beam on a target, ablating a portion of the target to eject a plasma of the target substance, ionizing part of the plasma with the laser, and positioning a substrate to collect the ions to form a layer of material on the substrate.

USP 4,986,214 ("ZUMOTO"; 1/91; 118/722) discloses a thin-film forming apparatus capable of forming thin diamond films. The process is a laser CVD process in which thin-film forming gases are optically dissociated by high energy photons released form an ultraviolet laser beam.

USP 4,874,596 ("LEMELSON"; 10/89; 423/446) discloses directing an intense radiation beam into a cavity supporting a small quantity of material to be reacted on. Two or more intense radiation beams, such as generated by one or more lasers or electron guns, are directed against a particle or pellet of material from opposite directions, causing shock waves which collapse against the pellet material, transforming it into another form. The pellet or particles may comprise carbon, which is converted to diamond by the intense heat and force of the shock wave(s).

USP 4,849,199 ("PINNEO"; 7/89; 423/446) discloses suppressing the growth of graphite and other non-diamond carbon species during the low pressure deposition of carbon to form diamond. The graphite or other non-diamond species is vaporized using incident radiative energy sufficient to vaporize graphite but insufficient to damage the substrate. The growth of graphite and other non-diamond species is suppressed during deposition of diamond by exposing growing surfaces to incident radiative energy of a wavelength sufficient to selectively photolyze non-diamond carbon-carbon bonds formed at the surface of the growing diamond. As is noted in the patent, high

WO 95/20253

PCT/US95/00782

pressure processes for synthesizing diamond all tend to suffer from the growth of graphite, which eventually causes diamond growth to cease. A low pressure method is disclosed in the patent whereby growth of graphite and other non-diamond carbon species is suppressed by evaporation or selective photolysis. In one method disclosed in the patent, the graphite or other non-diamond carbon species is vaporized using incident radiant energy sufficient to vaporize graphite but insufficient to damage the substrate. In another method disclosed in the patent, the graphite or other non-diamond carbon species is selectively photolyzed, such as, by the use of laser energy of appropriate wavelength. The methods of the patent are intended to function in conjunction with a plasma enhanced chemical vapor deposition process (PECVD) to grow diamonds on seed crystals, requiring a carbon source gas. The use of a laser is suggested to vaporize the graphite and non-diamond carbon species as they form upon the diamond growing surface, with the caveat that the laser energy should be low enough to avoid any substantial physical or chemical damage to the substrate, particularly if the substrate is other than a diamond seed crystal. It is further suggested in the patent that control of graphite growth over a large diamond crystal or substrate area may be achieved by scanning a tightly focused beam over the entire area.

USP 4,522,680 ("OGAWA"; 1/85; 156/624) discloses a method of producing diamond crystals comprising providing a pressure-resistant body having a nucleus of a starting material being crystallized in the inside thereof. The nucleus is applied with an energy which is capable of passing through the pressure-resistant body and being absorbed by the starting material, by which the nucleus is heated and melts. The melt is then gradually cooled under pressure to form crystals. A laser beam or high frequency induction heating technique is used for heating the nucleus.

WO 95/20253

PCT/US95/00782

5 USP 5,176,788 ("KABACOFF"; 1/93; 156/603), entitled METHOD
OF JOINING DIAMOND STRUCTURES, discloses the use of pulsed laser
light to join diamond structures together. The process includes
forming a layer of opaque non-diamond material between the two
diamond surfaces to be joined, pressing the diamond surfaces
together, using the pulsed laser light to quickly melt all the
opaque nondiamond carbon material before a significant amount
of heat is lost through the diamond surface, then allowing the
resulting carbon melt to cool and solidify as polycrystalline
10 diamond which grows homoepitaxially from the diamond surfaces,
bonding those surfaces together.

15 USP 4,892,751 ("MIYAKE"; 1/90; 427/34) entitled METHOD AND
APPARATUS FOR FORMING A THIN FILM discloses a technique wherein
a gas which contains an element used to constitute a desired
thin film as at least a part of its constituent elements of a
condensed solid layer of this gas is irradiated with a high
output power laser (e.g., KrF excimer) beam to dissociate the
gas of the solid layer of the gas and thereby locally produce
a plasma, and a substrate is irradiated with reactive particles
20 produced in the plasma, thereby obtaining a highly-pre high-
quality thin germanium (Ge) film employed in a semiconductor
device. In MIYAKE, a silicon substrate (10) is disposed so that
its surface (plane) is parallel to the optical path of the laser
beam. A substrate-heating heater (11) is provided at the back
25 of the substrate, to maintain the temperature of the substrate
at 400 °C, in a manner analogous to CVD processes. Generally,
the laser is used to create a plasma, but does not act directly
upon the substrate.

30 USP 4,681,640 ("STANLEY"; 7/87; 148/1.5) entitled LASER-
INDUCED CHEMICAL VAPOR DEPOSITION OF GERMANIUM AND DOPED-
GERMANIUM FILMS discloses forming germanium and doped-germanium
polycrystalline films using a tunable, continuous wave CO₂ laser

WO 95/20253

PCT/US95/00782

which delivers infrared laser radiation in the range of 10.4 or 9.4 μm to implement photolytic, laser-induced chemical vapor deposition. A starting material, such as tetramethylgermane (TMG) which has a high vapor pressure and which does not have a frequency of vibration resonant with the output of the CO₂ laser is used in the presence of a "sensitizer" - a substance which absorbs the laser energy and then subsequently reacts with a transfer energy to the TMG.

USP 5,080,753 ("DOLL"; 1/92; 156/609), entitled LASER DEPOSITION OF CRYSTALLINE BORON NITRIDE FILMS, discloses using a KrF excimer laser to ablate a boron nitride target incident to causing boron nitride to deposit on a single crystal silicon substrate which is pre-heated to approximately 400°C and maintained at that temperature throughout the ablation and deposition process. In DOLL, the laser does not act directly on the substrate.

USP 5,096,740 ("NAKAGAMA"; 5/92; 427/53.1), entitled PRODUCTION OF CUBIC BORON NITRIDE FILMS BY LASER DEPOSITION, discloses irradiating an excimer laser on a target containing boron atoms (and optionally, nitrogen atoms), and depositing cubic boron nitride on a substrate which is placed to face the target. In NAKAGAMA, the laser does not act directly on the substrate. Typically, the substrate for growing CBN (cubic boron nitride) is limited to silicon.

USP 4,701,592 ("CHEUNG"; 10/87; 219/121LT), entitled LASER ASSISTED DEPOSITION AND ANNEALING, discloses using a Q-switched Nd:YAG laser, splitting its output beam, directing a first output beam to a source (target) of material to evaporate the material, and directing the second output beam to the substrate. The evaporated target material forms a film on the substrate. The substrate is placed at a location to avoid "splashing" (eruptions of hot solid particles or liquid droplets from the

WO 95/20253

PCT/US95/00782

target) from the target, and the second output beam is used to anneal the deposited (on the substrate) film (of condensed material). The process is especially useful for advanced electronic device applications, especially for incorporating
5 films into silicon integrated circuit structures.

SHORTCOMINGS OF PRIOR ART TECHNIQUES

The processes described hereinabove can generally be characterized as "deposition" techniques, whereby material (e.g., diamond) is formed and deposited onto the surface of a
10 substrate. At best, using these processes, a molecular bond will be formed between the deposited coating and the substrate, and such a molecular bond will exhibit limited "adhesion" (mechanical keying) between the deposited coating and the substrate. In certain applications, such as in coating cutting
15 tool inserts, the adhesion of a diamond coating to the substrate is profoundly non-trivial. Moreover, the surface finish of the deposited coating is such that various post-finishing steps are required to achieve a desired finish on the coated part.

Prior art coating processes also tend to be limited to
20 forming a thin film (or layer) on a substrate. This is somewhat analogous to rain falling on a lawn and freezing. The resulting ice layer is relatively hard, but is thin, and there is an abrupt transition of hardness from the thin ice layer (coating) to the underlying grass (substrate). This will result in
25 extremely poor stress distribution, as a result of which the thin layer of ice is subject to cracking when stress is applied. Generally, the thickness of the coating will reflect upon the stresses that build up in the coating.

Generally, prior art processes exhibit low rates of
30 deposition, require significant pre-heating and post-cooling of the substrate, cannot be carried out in an ambient environment

WO 95/20253

PCT/US95/00782

(thereby severely limiting the size of a substrate that can be coated), are ill-suited to coating certain substrates (e.g., cobalt-containing substrates), and result in coatings with poor adhesion (to the substrate) and requiring post-process finishing steps (to acquire a desired surface finish on the coated substrate). These processes also require surface preparation and seeding.

RAMAN SPECTROSCOPY

An exemplary tool for characterizing (analyzing) a diamond (or DLC) coating (or film) deposited on a substrate is Raman spectroscopy. As diamond technology has advanced, Raman spectroscopy has emerged as one of the principal tools for characterizing diamond materials. Cubic diamond has a single Raman-active first order phonon mode at the center of the Brillouin zone. Natural diamond single crystals can be identified by a single peak at 1332 cm^{-1} . Synthetic diamond films often exhibit another peak at about 1550 cm^{-1} , for which a satisfactory explanation is yet to be developed. Semi-quantitative analysis of a sample, based solely on Raman spectroscopy, is difficult. However, there are some literatures in which people assume that the 1550 cm^{-1} peak is due to graphite, the sensitivity of which is about two orders of magnitude higher than that of diamond. Diamond-like carbon (DLC) always exhibits these two peaks (1332 cm^{-1} and 1550 cm^{-1}). Due to the sensitivity factor, it has generally been accepted that the 1332 cm^{-1} peak is adequate proof of the existence of diamond material in a sample. However, many synthetic diamond materials do not exhibit this peak at all, exhibiting instead tiny broad features superimposed on significant background luminescence. In general, the sensitivity (sharpness) of the diamond peak may depend to a certain degree on its grain size - namely, the smaller the grains, the lower the sensitivity and the broader the peak will be. Moreover, diamond films deposited on hard substrates such as alumina or carbides often exhibit a

WO 95/20253

PCT/US95/00782

shift, as large as 15 cm^{-1} , in the peak due to the stress state of the film. Although a useful tool for characterizing a diamond or diamond-like coating fabricated on a substrate, Raman spectroscopy cannot be relied upon as dispositive of the "quality" of the coating. Ultimately, a coated cutting tool should be tested in its intended application (e.g., in a milling machine, lathe, drillpress, or the like, actually cutting a workpiece) at a range of feed rates, for tool life, flaking and resulting workpiece finish, for a given one or more workpiece materials (e.g., aluminum alloys, steel alloys, composite materials). A "successfully" coated cutting tool may also be defined by its ability to perform "dry" (no lubricant or cutting oil) machining.

RAPID PROTOTYPING

The surface treatment technique of the present invention is also useful in the field of rapid prototyping.

Prior art methods for rapidly making an object provides limited engineering evaluation and are not suitable for production use or prototyping. Prior art technology uses photopolymers or extruded materials, among other non-metallic techniques, to produce rapid prototype plastic parts or laser sintered powders to produce metal parts. All of these methods produce relative rough parts of limited utility.

For example, a stereolithography apparatus (SLA) is typically used in rapid prototyping system. Stereolithography is a process by which three dimensional objects are fabricated from thin layers of hardened cured liquid polymers. Current rapid prototyping systems make an object by selectively hardening or cutting layers of material into a shape defined by CAD data. Typically, ultraviolet, argon-ion, or other type of laser is used to harden the polymer. The CAD data mathematically represent the shape of the object to be produced as a series of

WO 95/20253

PCT/US95/00782

sequential thin layers.

Several publications have emphasized the importance that rapid-prototyping (RP) technologies will have towards improving manufacturing systems and reducing costs. Furthermore, these articles identify the limitations that exist with the current art. In two recent publications, Manufacturing Engineering (Published by SME, pp. 37-42, November 1993) and Plastics Technology (pp. 40-44, January 1994), the respective authors emphasize the magnitude of rapid prototype and manufacturing systems. Other articles, such as those related to laser sintering, are also indicative of the state of the art in rapid-prototyping.

Generally, prior art rapid prototyping techniques make an object by selectively cutting layers of material into a shape defined by the CAD data. As noted in Manufacturing Engineering (November 1993), the "goal of current RP [rapid prototyping] technologies is prototype materials that provide higher strength at elevated temperatures. The industry desires full metal molds (without using sintered materials) so as to effectively analyze the object." Furthermore, this article notes that producing parts directly will be the ultimate step in rapid prototyping. Also, the article emphasized that the key will be materials and that although some experimental rapid prototyping systems are working with molten metals and metal powders, they are still far from high-strength, fully dense metals.

The following illustrates prior art methods for fabricating an object (e.g. Rapid Prototyping). Attention is directed to the following U.S. Patents, incorporated by reference herein, as indicative of the state of the art of stereolithography and object fabrication:

USP 5,260,009 ("System, Method, And Process For Making 3D

WO 95/20253

PCT/US95/00782

Objects");

USP 5,256,340 ("Method Of Making A 3-D Object By Stereolithography");

5 USP 5,248,456 ("Method And Apparatus For Producing Stereolithographically Produced Objects);

USP 5,247,180 ("Stereolithographic Apparatus And Method Of Use"); and

USP 5,236,637 ("Method And Apparatus For Production Of 3-D Objects By Stereolithography).

10 The use of a laser in producing prototype parts is described in USP 5,017,317 ("MARCUS"; 5/91; 264/81), entitled GAS PHASE SELECTIVE BEAM DEPOSITION, which discloses a computer controlling a directed energy beam, such as a laser, to direct
15 the laser energy into a chamber substantially containing a gas phase of a material sought to be deposited to preferably produce photodecomposition or thermal decomposition of the gas phase and to selectively deposit material within the boundaries of desired cross-sectional regions of a part being fabricated. For each
20 cross-section, the aim of the beam is switched on to deposit material within the boundaries of the cross-section. Each subsequent layer is joined to the immediately preceding layer to produce a part comprising a plurality of joined layers.

WO 95/20253

PCT/US95/00782

DISCLOSURE OF THE INVENTION

5 It is therefore an object of the present invention to provide an improved technique for applying (fabricating) a coating, particularly a diamond (or DLC) coating to (on) a substrate, such as a cutting tool insert, particularly to a cutting tool insert that contains a commercial range of cobalt or to a round cutting tool.

10 It is a further object of the present invention to provide a technique for applying a coating to a substrate in an ambient (non-vacuum) environment.

15 It is a further object of the present invention to provide a technique for applying a coating to a substrate without heating (or pre-heating) the entire substrate, while controlling the thermal balance of the treatment, without adversely affecting the entire mass of the substrate.

It is a further object of the present invention to provide a technique for forming a diffusion bonded coating on a substrate.

20 It is a further object of the present invention to provide a technique for treating a substrate of all steel alloys, including stainless steels, nonferrous materials or alloys, as well as other materials, such as ceramics and polymers.

25 It is a further object of the present invention to provide a technique for forming coatings having tailorable shapes, thicknesses, and compositions.

It is a further object of the present invention to provide a technique for treating a substrate in a manner which does not require post-process finishing.

WO 95/20253

PCT/US95/00782

It is a further object of the present invention to provide a technique for treating a substrate in a truly heteroepitaxial manner, such as for synthesizing diamond, DLC, or other crystalline materials.

5 It is a further object of the present invention to provide a technique for treating substrates having complex geometry.

It is a further object of the present invention to provide a technique for fabricating a tool or insert, especially a cutting tool.

10 It is a further object of the present invention to provide a technique for coating a substrate such a cutting tool or insert, especially with diamond and diamond-like coatings, as well as with other materials, in a manner that is robust with respect to carbide, even with relatively high cobalt
15 concentrations, useful for High Speed Steel, and ceramic, DLC on plastics (barrier coatings, etc.), and other cutting tool materials, and in a manner that can be performed at low temperatures and pressures.

20 It is a further object of the present invention to provide a technique for improving the adhesion of a coating to a substrate, especially diamond (and DLC) coatings, as well as with other materials, in a manner that is robust with respect to carbide, and in a manner that can be performed at low temperatures and pressures.

25 It is a further object of the present invention to provide a technique for treating the surface of a substrate in a manner that will provide a diffusion bonded composite material below the surface of the substrate.

WO 95/20253

PCT/US95/00782

It is a further object of the present invention to provide a technique for treatment and fabrication of materials to produce an object having a desired composite material, such as diamond, DLC, Cubic Boron Nitride (CBN), B_4C , SiC , TiC , Cr_3C_2 ,
5 TiN , TiB_2 , Si_3N_4 and cCN , niobium, carbide, titanium nitride, aluminum nitride, etc..

It is a further object of the present invention to provide a technique for fabricating "designer" coatings on a substrate.

It is a further object of the present invention to provide
10 a system that can produce useful metal, ceramic, and composite parts to a final state in a manner not requiring any post-process (outside the system environment) finishing and exhibiting enhanced physical properties by virtue of advanced composite materials not capable of being produced by other
15 currently known means.

It is another object of the invention to provide a technique for pre-treating (preparing) a substrate for subsequent coating by the techniques of the present invention or by prior art coating techniques.

It is another object of the present invention to provide
20 a technique for surface treating a substrate, without requiring a separate and distinct pretreatment step to characterize the surface of the substrate - in other words, performing pretreatment in conjunction with (in situ) fabricating a coating.

According to the invention, energy such as three distinct
25 laser beams from three distinct lasers are directed at the surface of a substrate to treat the surface of the substrate. The process parameters and interactions of the three lasers are controlled to achieve a desired effect on and/or below the
30 surface of the substrate. The process parameters include:

WO 95/20253

PCT/US95/00782

- the wavelength of each laser;
- the operating mode (e.g., pulsed, super-pulsed or continuous wave), including pulse width and frequency, for each laser;
- 5 • the output power of each laser;
- the energy of each laser;
- the angle of incidence on the surface of the substrate for each laser beam;
- the cross-sectional shape and size of each laser beam;
- 10 and
- the sequence (timing relationship) for directing the laser beams at the surface of the substrate.

For example, one or more constituent (native) elements disposed in a sub-surface region of the substrate may be mobilized, at corresponding one or more rates, and moved towards the surface of the substrate to produce a concentration gradient of the one or more constituent elements in a sub-surface zone. Further, selected amounts of a selected portion of the constituent elements may be separated and vaporized in a controlled manner. The one or more constituent elements of the substrate are considered to be a "primary" source of material for the process.

According to an aspect of the invention, the vaporized one or more constituent elements are reacted, immediately above the surface of the substrate, to modify the physical structure and properties of the vaporized one or more constituent elements to produce a composite material which is subsequently be diffused back into the substrate.

At an appropriate point in the process, which may be from the commencement of the process, one or more secondary sources containing secondary elements can be introduced into the reaction system occurring immediately above the surface of the

WO 95/20253

PCT/US95/00782

substrate. For example, carbon within the substrate can be mobilized, vaporized and reacted, and augmented with a secondary source of carbon dioxide providing additional carbon to the reaction system, to form a diamond or diamond-like carbon coating on the substrate.

A significant advantage of the invention accrues from the metallurgical changes occurring within the surface of the substrate. By diffusing reacted constituent elements back into the substrate, and/or by diffusing reacted secondary elements into the substrate, a diffusion zone (also referred to herein as transition zone) within the substrate will exhibit a gradient of material composition that transitions from pure substrate to pure coating. This will provide not only an intimate diffusion (e.g., metallurgical) bond between a coating fabricated on the substrate and the substrate itself, but will also provide a smooth (relatively non-abrupt) transition for physical stresses imposed on the substrate coating.

According to the invention, two distinct diffusion zones can be created within the substrate - a primary conversion zone well within the substrate, and a secondary conversion zone between the primary conversion zone and the surface of the substrate. For example, to fabricate an approximately 3 mm thick layer (coating) of diamond on a steel or cemented carbide substrate, the primary conversion zone could be approximately 0.75 mm deep, and the secondary conversion zone could be approximately 0.25 mm thick.

According to a feature of the invention, selected areas of the substrate are suitably treated with the three lasers, or with at least one laser and another energy source (e.g., an electron beam, an x-ray beam, etc.) emits a controllable beam. By "selected areas" it is meant that an area substantially less than the entire surface area of the substrate can be treated,

WO 95/20253

PCT/US95/00782

without treating the remainder of the surface. It will be understood, however, that a sequence of selected areas can be treated, in a serial or parallel manner, up to and including treating the entire surface (or surfaces) of the substrate.

5 According to the invention, the activity performed during each step of the process can be controlled by suitable means such as a CNC control station. The operating parameters of the laser, and associated optics, may be configured to achieve any desired treatment at any moment of time.

10 In an exemplary embodiment of the invention:

 • a first of the three lasers is an ultraviolet laser, such as a pulsed excimer laser, operating at either 192nm, 248nm, or 308nm, with a power output of tens of (0-200) watts (W), with a pulse energy of up to 500 mJ (millijoules), a pulse length of
15 up to 26 nanoseconds (ns), and a repetition rate of up to 300 Hz (Hertz);

 • a second of the three lasers is a Nd:YAG laser, operating at 1.06 microns in a continuous (CW) or burst mode, or Q-switch with a power output of hundreds of (0-1500) watts, with a pulse
20 energy of up to 150 J (Joules), a pulse frequency of up to 1000 Hz, a pulse length of up to 20 milliseconds (ms), and (in a pulse/burst mode) a pulse stream duration of up to 5 seconds;

 • a third of the three lasers is a CO₂ laser operating at a wavelength 10.6 microns, with a output power on the order of
25 500-10000 W, a pulse frequency up to 25 Khz, a pulse up to 25 microseconds, a super-pulse frequency up to 20 Khz, and a super-pulse width up to 500 microseconds.

In an exemplary application of the substrate treatment technique of the present invention:

30 • the substrate is carbon steel;
 • the constituent element of interest is carbon;
 • the secondary element, if utilized, may be carbon,

WO 95/20253

PCT/US95/00782

depending on the treatment, the desired coating thickness, and whether the substrate is high carbon steel or low carbon steel;

• the resulting conversion zone depth "d" is approximately 1.0 mm (including an approximately 0.25 mm secondary conversion zone); and;

• the resulting diamond coating thickness "t" is approximately 3 mm (or approximately three times the depth of the conversion zone).

In another exemplary application of the substrate treatment technique of the present invention, the constituent element is titanium, the secondary element is nitrogen, carbon or boron, and the resulting coating is titanium nitride, titanium carbide or titanium diboride, respectively.

Other applications (i.e., substrate materials, composites, secondary sources, and the like) of the techniques of the present invention are intended to be within the scope and spirit of this disclosure.

According to a feature of the invention, the energy directed at the substrate can advantageously be employed to cause (or to control) physical stresses in the coatings being fabricated, and that by advertently inducing such stresses, crystalline growth may be controlled (accelerated) to substantially increase the growth rates over the prior art.

According to a feature of the invention, the energy directed at the substrate can advantageously be employed to achieve any desired topography (texture) on the surface of the substrate, either as a final result (i.e., in-situ post finishing), or to prepare the surface (i.e., pre-treat the surface) for subsequent fabrication of a coating.

According to a feature of the invention, the secondary

WO 95/20253

PCT/US95/00782

source may include a doping element as one of the secondary elements. For example, a diamond or DLC coating could be doped for use, for example, a semiconductor application.

According to a feature of the present invention, an electrically bias may be applied to the substrate to control the orientation of crystal growth on the substrate, or on an already formed coating.

An advantage of the present invention is that it need not be performed in a vacuum. However, it is preferred that the reaction zone on the substrate is shielded by a shielding gas such as nitrogen or argon. This is not to say, however, that the process cannot be carried out in a vacuum. The process, or portions thereof can be used in conjunction with existing CVD and CVD-type processes to eliminate some of the limitations thereof. For example, rather than heating the entire substrate to drive a deposition reaction, the energy can be brought to bear upon (directed at) selected areas of the substrate, and can be scanned in any pattern on the surface of the substrate, to fabricate any desired "profile" (e.g., composition, thickness, shape) or pattern of coatings on the substrate. This will avoid many of the problems associated with heating the entire substrate, and will provide for results that are not otherwise obtainable with such processes (without masking the substrate).

Various designs (embodiments) of nozzles for introducing secondary elements in gaseous form, and for introducing shielding gases are disclosed herein.

Further according to the invention, the substrate (workpiece) is moved relative to the energy sources (e.g., lasers), or vice-versa, in order that the depth of the conversion zone and the thickness of the coating fabricated on the substrate can be controlled, from location-to-location

WO 95/20253

PCT/US95/00782

across the surface of the substrate.

Further according to the invention, the depth "d" of the conversion zone is controlled to a selected depth, by selecting any or all of the following: intensity, duration, profile and incidence angle of the laser beams.

Further according to the invention, technique can be controlled so that a multi-layered coating, each layer thereof having a desired composition, can be fabricated on a substrate.

Further according to the invention, the technique can be controlled so that multiple conversion zones may be created within the substrate.

The present invention exhibits several advantages over existing coating techniques, including:

- providing a continuous reaction system at selected (discrete) areas of the substrate
- a fabricated composition may be either "truly heteroepitaxial" and/or homoepitaxial; for example, a fabricated heteroepitaxial fabricated composition may develop into a homoepitaxial fabricated composition (e.g., the coating, or a subsequent coating when the composition is SP^3 carbon-bonded).

The techniques of the present invention allow for growth of a material on another underlying material without limitation as to crystal orientation, lattice structure, direction of growth, materials, etc. In other words, the material being fabricated is not limited (unrestrained) by properties of the material or substrate upon which it is being fabricated.

- any lattice structure may be formed as a coating on the surface by choosing an appropriate nucleation material and causing an appropriate species in the material of the substrate to enter the Preliminary Vapor Phase (PVP);
- the process may be performed without CVD processes,

WO 95/20253

PCT/US95/00782

without a vacuum, and without a target material;

- the process may be performed in ambient atmospheric conditions;

- the process may be performed without preheating the substrate;

- the process is continuous, and allows a composition of any desired depth to be formed below the surface of the substrate, and a composition of any desired thickness to be formed on and above the surface of the substrate;

- the bonding is deeper and provides for greater adhesion than the processes of the prior art;

- the coating can be formed on a substrate of virtually any size and shape, including very large substrates. There is virtually no limit to the thickness or area of composition formed by the process;

- treating a substrate to form a diamond or DLC surface maybe accomplished without affecting the original volume of the substrate.

Optics (beam delivery system) may be interposed between the lasers and the surface of the substrate so that the beams emitted by the lasers are either focused or diffused or otherwise (e.g., their profile and dimension) altered.

The secondary element is introduced into the reaction system by any of a number of known means, such as by spraying, dispersing, depositing, ablating, or by any other known means, and may be in the any suitable form such as a liquid, a gas, a solid, a plasma, a powder, or the like.

For example, a gaseous secondary element may be introduced into the reaction system using a pressurized nozzle (jet) that is designed to deliver the gaseous secondary element in an envelope of another (e.g., inert) gas which will focus (direct) the delivery of the secondary element by helically-controlled

WO 95/20253

PCT/US95/00782

swirling of the gases exiting the nozzle (jet). In this manner, the secondary element can be directed to the same selected area of the substrate as the incident energy beam.

5 According to a feature of the invention, the gaseous secondary element and the enveloping gas can both serve as secondary elements in the reaction.

A target, such as a graphite source, may be contained outside of or within the nozzle (jet) and irradiated by a energy source and subsequently introduced into the reaction system.

10 The secondary element may also be selected to serve as a "shield" (from the environment, without necessitating the use of a vacuum) for the process when a secondary source is not needed (see, e.g., Step C, F and H in the process flow, described hereinabove), in which case the secondary element (and
15 the enveloping gas) may be a clean or inert gas.

According to conventional usage, growth of a material upon itself, while retaining the crystalline nature of the underlying substrate is called "homoepitaxy". Growth of a dissimilar material onto a substrate, while retaining the crystal
20 orientation of the substrate is called "heteroepitaxy". As used herein, the term "truly heteroepitaxial" is used to convey the notion of synthesizing a material on an underlying, dissimilar material, irrespective of crystal orientation, and is intended to distinguish over systems (such as CVD or PVD systems)
25 requiring seeding of the material or otherwise providing nucleation sites to be synthesized, which are considered to be "homoepitaxial".

The techniques of the present invention are useful for treating a substrate with, and for coating a substrate with any
30 of a number of materials.

WO 95/20253

PCT/US95/00782

The techniques of the present invention are useful for treating virtually any size or shape substrate, such as large flat sheets, large formed sheets, piston rings, cylinder liners, spray nozzles, the insides of long cylindrical elements, valve seats, and the like.

The techniques of the present invention are useful for treating substrates of virtually any material composition, including superconductive materials.

The techniques of the present invention are truly heteroepitaxial, allowing for a coating to be fabricated in virtually any orientation on the surface of a substrate or previously formed coating, including "L"-shaped coatings and coating structures extending initially perpendicular to, then parallel to the surface of the substrate.

The techniques of the present invention facilitate creation of a conversion zone below the surface of a substrate, and the conversion zone can function as a support for enhanced diffusion bonding a coating layer fabricated on the substrate.

Vis-a-vis a coating fabricated on the surface of the substrate, such as a diamond coating, the techniques of the present invention facilitate the formation of such a coating at rates and at thicknesses which cannot be achieved using prior art coating processes. For example, a coating can be fabricated at a rates exceeding 100 μm per hour, including in excess of 1 mm per minute, 3 mm per minute and 10 mm per minute. Coatings with final thicknesses (t) exceeding 100 μm , including in excess of 1 mm, 3 mm and 10 mm can be fabricated.

Vis-a-vis the treatment of a substrate to form a conversion zone of composite material, the techniques of the present

WO 95/20253

PCT/US95/00782

invention facilitate the formation of such a conversion zone at rates and at depths 30 μm per hour, including in excess of 0.5 mm per minute, 1 mm per minute and 3 mm per minute. Conversion zones with final depths (d) exceeding 30 μm , including in excess of 0.5 mm, 1 mm and 3 mm can be fabricated.

The techniques of the present invention are continuous, overcoming the limitations of batch processing that are found in the prior art. Substrates having dimensions in excess of six inches, including greater than 8 inches, greater than 10 inches, greater than 30 inches, and greater than 100 inches can successfully be treated with the techniques of the present invention.

The techniques of the present invention are useful for treating a substrate to prevent corrosion, erosion and the like, and to create a chemically-inert surface on a partial area or the entire substrate.

An advantage of the low temperature (no pre-heating) techniques of the present invention is that the substrate will retain dimensional stability during treatment, and will not lose its underlying hardness (e.g., temper, in steel).

Generally, as described herein and in the parent cases, a diamond or diamond-like carbon coating (as well as a coating of another material) may be formed on a substrate without the addition of materials other than those (e.g., carbon constituent element) which inherently exist within the substrate. The coating which is formed exists not only on the surface of the substrate, but also beneath the surface, and is characterized by a diffusion bond which is formed between the coating and the substrate. The process can be used to form a diamond coating, a DLC coating, or another crystalline material coating. The process is unique in that it may be carried out in ambient

WO 95/20253

PCT/US95/00782

pressure, requiring neither a vacuum nor high pressure. Moreover, the process may be carried out without appreciably heating the substrate.

The surface treatment technique of the present invention is applicable to treating any of a number of substrates, including metal and non-metal substrates (non-metal substrates include ceramics and polymeric substrates). Specific materials that can be treated, or introduced into the reaction system, include, but are not limited to:

- metals (B, Al, Ti, Nb, Ta, Cr, Mo, W, Re, etc.);
- graphite and carbides (C, B_4C , SiC, TiC, Cr_3C_2 , WC, niobium carbide, hafnium carbide, etc.);
- nitrides (BN, TiN, TaN, Si_3N_4 , hafnium nitride, aluminum nitride, etc.);
- boron and borides (B, TaB_2 , TiB_2 , WB, FeB, NiB, etc.);
- Silicon and silicides (Si, and the different silicides of Mo, Fe, Ni, etc.);
- oxides (Al_2O_3 , SiO, SiO_2 , etc.); and
- organic compounds (PTFE, Kevlar, Polyimides, Liquid Crystalline Polymers, Polyethyltetrahalate, etc.).

According to a feature of the invention, a substrate can be pre-treated (for subsequent fabrication of a coating) with one of the lasers. For example, a beam from an excimer laser is directed at the surface of a tungsten carbide substrate to remove grinding marks and contaminants, and to remove cobalt from the surface of the substrate. Other metallurgical changes in the substrate are readily induced during such pre-treatment such as by additions of reaction gases to change surface chemistry, if required.

According to a feature of the invention, the techniques of the present invention can be employed for rapid prototyping of an object. Generally, a three-dimensional object is "built" of

WO 95/20253

PCT/US95/00782

a sequence of fabricated coatings.

Other objects, features and advantages of the invention will become apparent in light of the following description thereof.

WO 95/20253

PCT/US95/00782

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated in and form a part of this specification, illustrate embodiments of the invention and, together with the description, serve to explain the principles of the invention.

Figure 1 is process flow diagram illustrating the techniques of the present invention.

Figure 2A is partial, side cross-sectional view of a substrate treated (coated) by the techniques of the present invention, particularly illustrating the formation of primary and secondary conversion zones within the substrate.

Figure 2B is partial, side cross-sectional view of a substrate treated (coated) by the techniques of the present invention, particularly illustrating the formation of multiple coating layers on the surface of the substrate.

Figure 3 is a generalized perspective view of a one embodiment of a system for performing surface treatment of a substrate, according to the present invention.

Figure 4 is generalized perspective view of another embodiment of a system for performing surface treatment of a substrate, according to the present invention.

Figure 5 is a cross-sectional view of one embodiment of a nozzle for introducing a secondary element to the substrate treatment system of the present invention.

Figures 5A and 5B are top plan and cross-sectional views, respectively, of another embodiment of a nozzle for introducing a secondary element to the substrate treatment system of the present invention.

Figure 6A is a stylized, cross-sectional view of a tungsten carbide substrate, according to the prior art.

Figure 6B is a stylized, cross-sectional view of the tungsten carbide substrate of Figure 6A, after pre-treatment according to the techniques of the present invention.

WO 95/20253

PCT/US95/00782

Figure 7 is a perspective view of a substrate treatment system, according to the present invention, showing three lasers directing energy (beams) through a nozzle towards a surface of a substrate.

5 Figure 8 is a cross-sectional view of a substrate supported on a pedestal, for surface treatment according to the present invention, particularly illustrating a flat plasma that may be formed according to the techniques of the present invention.

10 Figure 9 is a schematic view of the major components of a system, such as the system of Figure 7, according to the present invention.

Figure 10 is a graph illustrating a sequence of operating the various components of the system of Figure 7, according to an example of the present invention.

15 Figures 10A, 10B, 10C and 10D are graph, chart and graph, respectively, of operating parameters for an excimer, Nd:YAG and CO₂ laser, according to an embodiment of the present invention.

20 Figure 11A is a photomicrograph of a surface of a prior art tungsten carbide substrate prior to surface treatment, exhibiting grinding marks and surface contamination.

Figure 11B is a photomicrograph of the surface of the tungsten carbide substrate of Figure 11A, after the pre-treatment regime of the surface treatment process of the present invention.

25 Figure 11C is a photomicrograph of the surface of the tungsten carbide substrate of Figure 11B, after the coating regime of the surface treatment process of the present invention.

30 Figure 11D is a Raman spectrograph taken of the surface of the tungsten carbide substrate of Figure 11C, which was surface treated according to the present invention.

Figure 11E is a photomicrograph representation of a cross-section of the tungsten carbide substrate of Figure 11C, which was surface treated according to the present invention.

35 Figure 11F is a photomicrograph of a diamond coating

WO 95/20253

PCT/US95/00782

exhibiting 1,0,0 crystal orientation, fabricated according to the techniques of the present invention.

Figure 12A is a detailed view of beam cross-sections and intersection, according to an example of the present invention.

5 Figure 12B is a side view of a substrate being surface treated, according to an example of the present invention.

Figures 13A through 13H are views of tailorable coatings that can be fabricated on substrates, according to the present invention.

10 Figure 13I is a perspective view of a three-dimensional, physical object that can be fabricated using the coating techniques of the present invention, and demonstrates the truly heteroepitaxial nature of the techniques.

15 Figures 14A and 14B are perspective views of long tubular substrates being treated according to the techniques of the present invention.

Figures 15A and 15B are cross-sectional views of ball bearings that have been coated according to the techniques of the present invention.

20 Figure 16A is a side view of a round tool being surface treated, according to an embodiment of the present invention.

Figure 16B is a side view of a round tool being surface treated, according to another embodiment of the present invention.

25 Figures 16C and 16D are side and end views, respectively, of a round tool being surface treated, according to another embodiment of the present invention.

30 Figures 16E is a side view, respectively, of a round tool being surface treated, according to another embodiment of the present invention.

Figures 16F is a side view, respectively, of a round tool being surface treated, according to another embodiment of the present invention.

WO 95/20253

PCT/US95/00782

DETAILED DESCRIPTION OF THE INVENTION

As used herein, the term "surface treatment" means altering the metallurgy of a substrate, including "fabricating" one or more coating layers on the surface of a substrate or on a surface of a previously fabricated coating, as well as modifying the composition of the substrate in a sub-surface region ("conversion" or "transition" zone) below the surface of the substrate. Two surface treatment "regimes" are described -a "pre-treatment" regime in which the substrate is prepared for subsequent coating by any suitable coating technique, and a "coating" regime in which a coating is fabricated on the surface of the substrate. As used herein, the term "substrate" includes an article such as a flat or round cutting tool, and is also applicable to a selected area of the article receiving surface treatment. Generally, the coating technique of the present invention involves extracting and reacting a "constituent" (or "primary") element from the substrate, reacting it in a "reaction zone" immediately above the surface of the substrate, optionally introducing a "secondary element" from a "secondary source" to augment the reaction, and diffusing a "composite material" (the reacted material, having its physical structure, including phase, altered, modified, changed, and/or that has had another one or more elements added to it) back into the substrate. In this manner, in the transition zone there will be "artifacts" of the composite material and/or fabricated coating material evident, and the fabricated coating will be "diffusion bonded" to the substrate.

Reference will now be made in detail to the preferred embodiments of the invention, examples of which are illustrated in the accompanying drawings. While the invention will be described in conjunction with the preferred embodiments, it will be understood that the described embodiments are not intended to limit the invention to those embodiments. On the contrary,

WO 95/20253

PCT/US95/00782

the invention is intended to cover alternatives, modifications and equivalents, which are intended to be included within the spirit and scope of the invention as defined by the claims appended hereto.

- 5 In the main, hereinafter, examples of fabricating a diamond coating on a tungsten carbide cutting tool insert are discussed. However, as will be evident, the invention is not limited by these materials.

WO 95/20253

PCT/US95/00782

PROCESS FLOW CHART (Figure 1)

Figure 1 is a diagram showing the overall flow 100 of the techniques that can be implemented, according to the present invention. Generally, the techniques all involve directing
5 laser energy (preferably from three distinct lasers) at a surface of a substrate to drive a reaction system based on constituent elements, and introducing secondary elements at appropriate junctures into the reaction system. As will be evident, the process can proceed in various directions, and may
10 be terminated at various points in the process flow.

In a first process step (Step A), the laser energy is utilized to:

- mobilize one or more constituent elements in a sub-surface region (zone) of the substrate, at corresponding one or
15 more rates, and moves the one or more constituent elements towards the surface of the substrate to produce a concentration gradient of the one or more constituent elements in the sub-surface zone;
- separate (from other materials within the substrate) and
20 vaporize selected amounts of a selected portion of the one or more constituent elements in a controlled manner; and
- react the vaporized one or more constituent elements in a preliminary gas reaction (PGR) occurring immediately above the surface of the substrate to modify the physical structure and
25 properties of the vaporized one or more constituent elements. The combination of modified and unmodified constituent element(s) is a "composite material". This step (Step A) essentially prepares the substrate for further processing, as described with respect to Step B. The process may also be
30 terminated at this stage, as indicated by Step H.

In a process Step B, the composite material is diffused into the surface of the substrate creating a "conversion zone"

WO 95/20253

PCT/US95/00782

extending into the substrate from the surface of the substrate. This is essentially a process of passive diffusion from a greater concentration of composite material in the PGR to a lesser concentration of composite material in the substrate.

5 The process next proceeds in one of two directions (Steps C and D, described hereinbelow).

In a process Step C, the process can be stopped, at the point of having successfully formed a conversion zone exhibiting a controlled concentration of composite material. For example,

10 the composite material in the conversion zone may be diamond or DLC. As a general proposition, the production of a composite material, and its diffusion into the conversion zone, does not alter the volume of the substrate.

Alternatively, (i.e., to Step C), in a process Step D, the conversion zone can further be treated by repeating the steps of mobilizing, vaporizing and reacting (in a manner similar to Step A) the composite material within the conversion zone, or mobilizing, vaporizing and reacting the one or more of the constituent elements from the substrate, or both. In the case

20 of further treating the composite material within the conversion zone, the process acquires synergy and will proceed at a greatly increased rate (e.g. exponentially). This process is iterated to achieve any desired concentration of composite material at the surface of the substrate, and any desired gradient of composite material within the conversion zone.

25

At this point in the process, a coating can be fabricated on the surface of the substrate. The coating, or fabricated material, can have an entirely different chemistry than that of the conversion zone. To fabricate the coating, a secondary

30 source may (Step E) or may not (Step F) be introduced to the system.

WO 95/20253

PCT/US95/00782

In a process Step E, a "secondary" source (the substrate itself is considered the "primary" source) is activated to introduce one or more "secondary" elements (the one or more constituent elements of the substrate are considered to be "primary" elements) to the reaction system. The energy source is used, in this case, to fabricate a synthesized coating composition (such as diamond or diamond-like carbon) on the surface of the substrate. The synthesized coating composition is a fabricated material containing both the one or more secondary elements and the composite material, which may be the same as one another or different than one another.

As noted above (e.g., Step D), a conversion zone will be formed below the surface of the substrate. This conversion zone may comprise a primary conversion zone and a secondary conversion zone between the primary conversion zone and the surface of the substrate. Generally, the secondary conversion zone will have a relatively small depth, as compared with the primary conversion zone, and will have a greater concentration of the one or more secondary elements than are present in the primary conversion zone. The secondary conversion zone, in conjunction with the primary conversion zone, provides an important function vis-a-vis bonding, support and stress distribution for subsequent fabrication of a coating on the substrate. The conversion zone (primary and secondary) has an overall influence in defining the parameters required for bonding, support and stress distribution for a subsequent coating, if any, fabricated on the substrate. In this manner, a conversion zone having a depth " d " can be formed below the surface of the substrate, and a coating material of thickness " t " can be fabricated on the surface of the substrate.

For example, to fabricate an approximately 3 mm (millimeter) thick layer (coating) of diamond on a steel or cemented carbide substrate, the primary conversion zone could

WO 95/20253

PCT/US95/00782

be approximately 0.75 mm deep, and the secondary conversion zone could be approximately 0.25 mm thick.

Alternatively (i.e., to the Step E), in a process Step F, wherein a secondary source is not introduced to the system, a small amount of the composite material from the conversion zone is mobilized, vaporized and reacted (in a manner similar to the Step A) to form a secondary conversion zone below the substrate, which can further be reacted (by the energy source) to form a coating on the substrate. This results in a coating being fabricated on the substrate which is likely to be thinner than the coating that was fabricated using a secondary source (Step E). It is, however, entirely possible that there will be a sufficient amount of constituent element available in the substrate itself to fabricate a relatively thick coating on the surface of the substrate in the Step F.

For example, using a substrate of tungsten-carbide (e.g., 92%) in a cobalt matrix, the energy source will cause the tungsten and the carbide to disassociate into tungsten and carbon form, and the carbon will be the constituent element ("native" source) for fabricating a diamond or DLC coating on the substrate. Additionally, dissolved carbon in the cobalt matrix also provides a "native" source of carbon for the fabrication of diamond or DLC coating.

The surface treatment technique of the present invention is superior to prior art CVD (and PVD) processes in that in those processes cobalt will exhibit an undesirable graphite-forming influence in the system which will "poison" the system and inhibit the formation of a diamond coating or DLC coating.

Using the technique of the present invention, any graphite formed in the process will advantageously and continuously be converted to diamond in the diamond coating being fabricated.

WO 95/20253

PCT/US95/00782

Preferably, all of the available graphite is consumed by the process. However, it is not destructive of the process if a small amount of graphite remains unconverted into diamond.

5 In a process **Step G** (which follows **Step E** in the process flow), as a coating is fabricated on the substrate, a different (than the previously used) secondary source having different one or more secondary elements can be introduced to the reaction system. This will result in a multi-layer coating being fabricated on the substrate.

10 For example, starting with a tungsten carbide substrate, an overlying coating (layer) of titanium carbide can be fabricated, over which a layer of titanium nitride can be fabricated, over which a layer of diamond can be fabricated, by sequencing the introduction of secondary elements into the
15 reaction system.

By way of further example, a thick diamond coating could be overcoated with a thin coating of cubic Boron Nitride (CBN).

The process is also suitable for fabricating a coating of diamond on silicon nitride.

20 The process can also be employed to fabricate a composite structure of diamond and CBN, or vice-versa, or to fabricate a composite structure of diamond particles mixed with silicon carbide or silicon nitride.

25 As represented by a process **Step H**, it may be desirable in some instances to avoid (or minimize) diffusing the composite material back into the substrate (see **Step B**), in which case the process can be stopped after mobilizing, vaporizing and reacting the one or more constituent elements of the substrate in the **Step A**. This is advantageous for fabricating a very thin

WO 95/20253

PCT/US95/00782

coating on the surface of the substrate.

For example, it may be desired to form a thin coating of diamond or DLC on the surface of a substrate (e.g., a copper wire), or below the surface of the substrate, without affecting the original volume (e.g., dimensions) of the substrate. For example, material compositions of selected areas or the entire area of ball or roller bearing tracks or races may be enhanced without affecting their volume.

It is also possible that the process flow can proceed directly from the initial mobilizing, vaporizing and reacting (Step A) to the step (Step E) of introducing a secondary source to the reaction system. (This "bypass route" is considered a process step, and is shown as process Step I in the diagram of Figure 1).

For example, in order to fabricate diamond on a pure titanium substrate, it would be necessary to introduce carbon as a secondary element to the system (there being no carbon available as a constituent element in the substrate). The step of mobilizing, vaporizing and reacting the titanium from the substrate will serve to form a diffusion bond with the subsequently fabricated diamond or DLC coating.

For example, starting with a silicon substrate, carbon can be introduced by the secondary source to produce silicon with silicon carbide in the conversion zone. Then, the silicon carbide can be converted to diamond. Or, for example, nitrogen can be introduced by the secondary source to produce silicon with silicon nitride in the conversion zone and, if desired, the secondary source can be sequenced to provide carbon in the reaction system for forming a diamond or DLC layer over the conversion zone.

WO 95/20253

PCT/US95/00782

CONVERSION ZONE(S) (FIGURE 2A)

Figure 2A shows a cross-section of an exemplary treated substrate 200 that has been treated according to the techniques of the present invention, according to one or more of the process steps described with respect to Figure 1. Therein is shown a substrate 202 having a top surface 204, a secondary conversion zone 206 formed below the surface of the substrate, a primary conversion zone 208 formed underneath the secondary conversion zone 206, and a coating 210 that has been fabricated on the surface of the substrate. The treated substrate 200 could result, for example, from performing the process Steps A, B, D and E (of Figure 1). As noted above, the secondary conversion zone 206 will have a thickness (d_2) typically less than the thickness (d_1) of the primary conversion zone, and will exhibit a greater concentration of composite material than the primary conversion zone. In aggregate, the depth (d) of the conversion zones is $d_1 + d_2 = d$. The thickness of the fabricated coating is " t ".

MULTI-LAYER COATINGS (FIGURE 2B)

Figure 2B shows a cross-section of an exemplary treated substrate 220 that has been treated according to the techniques of the present invention, according to one or more of the process steps described with respect to Figure 1. Therein is shown a substrate 222 having a top surface 224, a first coating layer 226 of thickness " t_1 " formed atop the substrate surface (the primary conversion zones and secondary conversion zones are omitted from this figure, for illustrative clarity), a second coating layer 228 of thickness " t_2 " formed atop the previous (as viewed) surface of the first coating layer 226, and a third coating layer 230 of thickness " t_3 " formed on the top (as viewed) surface of the second coating layer 228. Such a treated substrate 220 could result, for example, from performing

WO 95/20253

PCT/US95/00782

the process Steps A, B, D, E and G (of Figure 1).

According to a feature of the invention, a multi-layer coating such as is shown in Figure 2B is readily fabricated. For example: the first coating layer 226 can be formed from a combination of a constituent element of the substrate and a first secondary element introduced into the reaction system by the secondary source; the second coating layer 228 can be formed from a combination of a constituent element of the first coating layer 226 and a second secondary element introduced into the reaction system by the secondary source; the third coating layer 238 can be formed from a combination of a constituent element of the second coating layer 226 and a third secondary element introduced into the reaction system by the secondary source. Depending on the application, any number of layers can be fabricated, having a predetermined material composition.

This demonstrates one aspect of the flexibility and controllability of the reaction system, namely, the nature and composition of a fabricated coating can easily be determined simply by the introduction of, in this case, a sequence of different secondary elements into the reaction system. As will become evident in the discussion that follows, there are many additional features of the technique of the present invention that allow a high degree of controllability and selectivity in the enhancement of material composition, including fabrication of coatings.

ENERGY SOURCE(S) (FIGURE 3)

Figure 3 illustrates, schematically, the operation of a surface treatment system 300, according to the present invention. Three separate and distinct lasers 312, 314 and 316 each direct a beam, via a respective beam delivery system (BDS) 322, 324 and 326 onto a surface 304 of a substrate 302. As

WO 95/20253

PCT/US95/00782

illustrated, the beams are directed to converge on a selected area 330 of the substrate, indicating that selected areas (each less than the entire surface) of a surface of a substrate can be treated. In order to treat the entire surface of the substrate, either (a) the selected area (330) must be equal to or greater than the total surface area of the surface of the substrate, or (b) a mechanism must be provided for causing relative motion between the substrate and the beams, to "scan" the selected treatment area across the entire surface of the substrate. In this figure, it is illustrated that the substrate can be moved relative to the beams, in the direction indicated by the arrow 332, thereby causing the selected area whereat the beams converge to move in an opposite direction indicated by the arrow 334 to surface treat an area greater than one selected area of the substrate. One having ordinary skill in the art to which the invention most nearly pertains will understand that various robotic/automated/positioning mechanisms can readily be employed for causing such relative motion between the substrate and the beams, and that the scanning path may be controlled in any suitable (desired) manner. For example, the substrate 302 may be held in a positioning mechanism, such as in the end effector (e.g., x,y,z) of a multi-axis robot, in which case it will be possible to move the substrate in any of the x, y and z directions, which is useful for treating substrates of complex geometry and/or multiple surfaces of a substrate. For a flat substrate, having a substantially planar surface, it is acceptable to move the substrate with a simpler mechanism, such as with an x-y positioning table. However, it may be necessary for specific applications desirable to control additional configurations, including controlling the focal points and angles of the beams. One of ordinary skill in the art to which the invention most nearly pertains will readily understand that such scanning of the beams themselves can be effected under computer control (with suitable galvos, or the like), and programmed to follow any desired path, dwelling on any portion

WO 95/20253

PCT/US95/00782

of the area of the surface of the substrate for any desired time and that the energy level and focal points can also selectively be controlled. For certain applications it may be desirable to have both a device for scanning the beams, as well as a multi-axis substrate positioning mechanism, to achieve the desired results. One advantage of using a robot-type mechanism for imparting motion to the substrate is that the same robotic mechanism can be used to pick (retrieve) substrates for surface treatment and to place (deliver) substrates after surface treatment. One of ordinary skill in the art to which the invention most nearly pertains will readily understand that such movement of the substrate can be effected under computer control, and programmed so that the beam will follow any desired path, dwelling on any portion of the area of the surface of the substrate for any desired time.

The laser energy sources 312, 314 and 316 can be focussed, diffused, converged, diverged, transported, or the like by interposing suitable known optical elements for achieving these functions in the path of the beam and which may be controlled by a computer numerical control. Such optical elements are generally shown as beam delivery systems (BDS) 322, 324, 326.

Each of the three lasers used in the surface treatment of the substrate contribute to the overall reaction being caused. Generally:

• a first one 312 of the lasers (LASER 1) is used to vaporize the constituent element (create a gas phase), and to break chemical bonds in the vaporized constituent element. The first one of the lasers is preferably an excimer laser operating, for example, at 192, 248 or 308 nm (nanometers). Such excimer lasers are useful for vaporizing any of a number of constituent elements. In most instances, the excimer laser will take a sole or primary (lead) role in causing the constituent element to vaporize, and in initiating the

WO 95/20253

PCT/US95/00782

preliminary gas reaction (PGR) above the surface of the substrate. In some instances, the excimer laser will be supported in these roles by another one (e.g., 314) of the lasers.

5 • a second one 314 of the three lasers (LASER 2) is used, primarily, to drive the diffusion function (e.g., Step B), and also balances the thermal gas reaction and the stoichiometric chemistry of the gas phase reactions. This laser is preferably a Nd:YAG laser, and normally assumes a supportive role (in a
10 manner of speaking) to the lead role of the excimer laser. In some instances (scenarios), the Nd:YAG laser will also aid in vaporizing the constituent component, especially in the context of bright (reflective) materials, and in some instances the Nd:YAG laser will assume the lead role and be supported by the
15 excimer laser (i.e., for some substrate and desired coating materials, the roles of the excimer and Nd:YAG lasers may be interchanged). Generally, by using both an excimer and a Nd:YAG laser, to initiate vaporization of the constituent element and to balance the reaction, there is an interaction
20 between the two lasers that keeps the reaction mechanism balanced out. It is advantageous, in any instance, to use both of the lasers to support the reaction. For example, if it is desired to form a diamond coating, the greater power and pulse capabilities of an excimer laser will normally take the lead in
25 initiating the gas phase reaction, and will be supported by the Nd:YAG laser.

 • a third one 316 of the three lasers (LASER 3), preferably a CO₂ laser, is used to balance the thermal, physical, gas and chemistry reactions occurring above the surface of the
30 substrate. The principal role of the CO₂ laser is to provide thermal balance, and to avoid there being a substantial thermal gradient in the reacted gases. The CO₂ laser will also provide a minimum temperature balance for the gas reaction, and will bias the temperature of the reaction. The CO₂ laser will also
35 provide synergy between the reaction occurring at the surface

WO 95/20253

PCT/US95/00782

of the substrate and the gas reaction occurring above the surface of the substrate. In certain instances (i.e., with certain substrate materials), the CO₂ laser could also be employed to initiate the reaction (i.e., take over the primary role of the excimer laser with respect to this function).

Although the lasers are shown in Figure 3 as directing their respective beams onto the selected area 330 of the substrate from different angles (an converging on the spot 330), it is within the scope of the present invention that the beams could be directed coaxially at the reaction zone. Generally, due to the synergy effected by the three lasers, they should all be directed at the same spot (330) on the substrate.

SECONDARY SOURCE(S) (FIGURE 4)

Figure 4 illustrates a surface treatment system particularly suited to introducing one or more secondary elements. In this figure, the three lasers (e.g., the three lasers 312, 314, 316 of Figure 3) are shown as one (combined) element delivering their beams through a beam delivery system (BDS) 412. The beams are directed at a selected area (compare 330) of a surface 404 (compare 304) of a substrate 402 (compare 302), and relative motion between the beam(s) and the substrate 402 is indicated by the arrows 432 and 434 (compare 332 and 334). In the surface treatment system 400 of Figure 4, there is also provided at least one secondary source (SECONDARY SOURCE 1) 420. There may be a plurality ("N") of secondary sources, as indicated by the secondary source (SECONDARY SOURCE N) 422. The one or more secondary sources introduce corresponding one or more secondary elements into the reaction system (constituent elements of the substrate are considered to be primary sources for the reaction), and the secondary elements may be in the form of a gas, a vapor, a powder, or other suitable form, to augment the reaction occurring in the reaction

WO 95/20253

PCT/US95/00782

zone immediately above the surface of the substrate. The secondary element is suitably provided by a nozzle (jet) adequate to direct a stream of the secondary element at the reaction zone, so that the secondary element(s) can contribute to the reaction that is being driven by the laser beams. It is preferred that the secondary element(s) be directed towards the same area (430) of the substrate whereat the laser beams are directed, but it is also possible to introduce the secondary source at another selected area on the substrate, or to simply "flood" the substrate (i.e., the entire surface of the substrate) with the secondary element(s). By introducing a secondary element to the reaction, a coating may be fabricated on the surface of the substrate, for example, as described with respect to Step E in the process flow diagram of Figure 1.

The secondary element is introduced into the reaction system by any of a number of known means, such as by spraying, dispersing, depositing, ablating, or any other known means, and may be in the any suitable form such as a liquid, a gas, a solid, a plasma, a powder, or the like.

For example, a gaseous secondary element may be introduced into the reaction system using a pressurized nozzle (jet) that is designed to deliver the gaseous secondary element in an envelope of another (e.g., inert) gas which will focus (direct) the delivery of the secondary element by helically-controlled swirling of the gases exiting the nozzle (jet). In this manner, the secondary element can be directed to the same selected area of the substrate as the incident energy beam. According to a feature of the invention, the gaseous secondary element (SS) and the enveloping (shielding) gas (SG) can both serve as secondary elements in the reaction. The secondary element may also be selected to serve as a "shield" (from the environment, without necessitating the use of a vacuum) for the process when a secondary source is not needed (see, e.g., Steps C, F and H in

WO 95/20253

PCT/US95/00782

the process flow, described hereinabove), in which case the secondary element (and the enveloping gas) may be a clean or inert gas. Depending on the treatment, a shielding function may not be necessary.

5

NOZZLE DESIGNS (FIGURES 5, 5A AND 5B)

10

Figure 5 illustrates an embodiment of a nozzle 500 suitable for introducing a gaseous secondary element (from a secondary source) to the reaction system. In this embodiment, the nozzle 500 is suitable for introducing three distinct gases - a gaseous secondary element (SS), a shielding gas (SG) and a "buffer" gas (BG).

15

The nozzle 500 is annular, having a ring-like body portion 508 and central axial opening 506. In use, the nozzle 500 is disposed above a surface of a substrate (SUBSTRATE) undergoing treatment. As shown, the three laser beams E1, E2 and E3 may be directed through the central opening of the nozzle, at the substrate.

20

In this nozzle embodiment 500, a shielding gas (SG, such as nitrogen) is introduced through a lower (closest to the surface of the substrate) inlet 530 of the nozzle, circulates through a annular runner 532 throughout the body of the nozzle, and is ejected via outlet ports 534 to the central opening (inner diameter) of the nozzle. A secondary source (SS, such as carbon dioxide) is introduced through an intermediate inlet 520 of the nozzle, circulates through a annular runner 522 throughout the body of the nozzle, and is ejected via outlet ports 524 to the central opening of the nozzle. Since the secondary source is ejected above (as viewed) the shielding gas, it is in a position to be reacted by the laser energy (E1, E2, E3), and to be enveloped (surrounded) by the shielding gas. A buffer gas (BG), analogous to a sensitizing agent, may be

25

30

WO 95/20253

PCT/US95/00782

introduced in conjunction with, such as above (as viewed) the secondary source. The buffer gas is selected (if necessary) to assist in the transferring energy from the laser beams to the secondary source, and may act as a buffer in breaking down the secondary source. As shown the buffer gas is introduced through an upper inlet 510 of the nozzle, circulates through a annular runner 512 throughout the body of the nozzle, and is ejected via outlet ports 514 to the central opening of the nozzle. Since the buffer gas is ejected from the nozzle above (as viewed) the secondary source, it is in a position to absorb laser energy (E1, E2, E3) for subsequent transfer to the secondary source gas. The nozzle 500 is disposed at a distance "h" above the substrate, which is established to provide sufficient time (i.e., propagation rate times distance) for the gas reaction to substantially complete itself between the nozzle and the substrate.

Figures 5A and 5B illustrate an alternate, preferred (e.g., for fabricating a diamond coating on a tungsten carbide substrate) embodiment of a nozzle 550 for delivering a secondary source (SS) gas and a shielding gas (SG) to the treatment system, and is generally similar to the embodiment 500 shown in Figure 5 in that the nozzle is annular and has a central opening through which the laser beams (shown by the single arrow labelled "BEAMS", in Figure 5B) can be directed through the gases towards the surface of the substrate (not shown) being surface treated. In this embodiment, the nozzle 550 is constructed as a "sandwich" of two flat, annular nozzle bodies 552 and 554, disposed one (552) atop the other (554). The top nozzle body 552 has an inlet 561 for receiving the secondary source (SS) gas, an annular runner 562 for circulating the secondary source gas evenly (in a fluid dynamic sense) throughout the top nozzle body, and a plurality of outlet ports 564 disposed about the inner diameter (ID) of the nozzle body 552. As best viewed in Figure 5A, the outlet ports are directed

WO 95/20253

PCT/US95/00782

tangentially, with respect to the axis of the nozzle body, to impart a swirling motion (e.g., clockwise, as viewed in Figure 5A) to the ejected secondary source gas. As best viewed in Figure 5B, the secondary source gas is preferable ejected from the nozzle body 552 flat (coplanar) with respect to the nozzle. This allows the secondary source gas to be as close to the incident laser beam energy (BEAMS) as possible, so that the reaction of the secondary source gas can commence immediately. As will be evident from discussion hereinbelow, the nozzle 550 is disposed at a sufficient distance ("h", see, e.g., Figure 7) above the surface of the substrate to permit the sought after reaction of the secondary source to occur. As shown in Figure 5B, the shielding gas (SG) is introduced through an inlet 580 in the lower nozzle body 554, circulates in a runner 582 throughout the lower nozzle body 554, and is ejected via a plurality of outlet ports 584 to the opening in the nozzle body. The openings in the two nozzle bodies 554 and 552 are concentric, and preferably of the same size as one another. As best viewed in Figure 5B, the outlet ports 584 for the shielding gas are directed downwards (as viewed), towards the substrate being treated. The outlet ports 584 should also be directed tangentially, with respect to the axis of the nozzle body, to impart a swirling motion (e.g., clockwise, as viewed in Figure 5A) to the ejected secondary source gas. This results in a "whirling vortex" (represented by the line 590) of shielding gas which will envelope and direct the secondary source towards the substrate. For simplicity of machining the nozzle bodies 552 and 554, the runners 562 and 582 are formed as troughs extending into the lower (as viewed) surfaces of the respective nozzle bodies. The top surface of the lower nozzle body 554 closes off the trough (runner 562) in the upper nozzle body 552, and a simple annular plate 592 having a central opening closes off the trough (runner 582) in the lower nozzle body 554.

WO 95/20253

PCT/US95/00782

PRE-TREATMENT (FIGURES 6A, 6B)

Generally, substrates will benefit from preparation of the surface sought to be coated. Grinding marks and contaminants may be present on the surface, and should be removed. Polishing and chemical etching are known processes for performing pre-treatment. Generally, chemical etching of a substrate requires the handling of hazardous chemicals, and result in toxic waste, each of which introduces added complexity to a system for coating a substrate. Moreover, each substrate composition would require its own chemicals to perform such etching. According to the present invention, substrates of various types are prepared for fabrication of a coating using the same laser(s) that are already in place for fabricating coatings.

According to a feature of the invention, the surface treatment system (e.g., 300) can be used not only for performing the surface treatment on the substrate, but can also be used to perform pre-treatment. Generally, this is a matter of controlling the process parameters of the lasers, vis-a-vis the gases.

Figures 6A and 6B illustrate how a substrate can be pre-treated, in conjunction with the surface treatment process of the present invention. The pre-treatment process can be performed prior to (i.e., separately from), or in conjunction with, the surface treatment process described with respect to Figure 1.

According to the present invention, the pre-treatment technique of the present invention can be used as a "precursor" to characterize the surface of a substrate for any subsequent coating process, including CVD and the like.

WO 95/20253

PCT/US95/00782

Generally, by way of example, as shown in Figure 6A, a tungsten carbide substrate 602 will exhibit grains 630 of tungsten carbide which are surrounded and covered by cobalt 632. As mentioned hereinabove, the presence of cobalt is somewhat problematic in the context of forming a diamond coating on a substrate. This is especially troublesome when the cobalt is present on the surface of the substrate. According to a feature of the invention, surface chemistry changes can be induced in such substrates, if required. For example, the chemistry of a tungsten carbide substrate can be altered to exhibit stable cobalt nitride.

According to a feature of the present invention, a substrate is pre-treated by using a one of the lasers (e.g., the excimer laser) to ablate cobalt (as well as some tungsten carbide) from the surface of the substrate, thereby exposing the tungsten carbide grains 634, and performing other significant metallurgical functions described in greater detail hereinbelow. Moreover, the cobalt can also be reacted to form a stable cobalt nitride. The cobalt can be ablated and some WC and Co can also be reacted to form stable carbon nitride or cobalt nitride. Nitrogen can be introduced to form cobalt nitride, if desired, during pre-treatment, to change the surface chemistry of the substrate, to form stable cobalt nitride or carbon nitride to assist in crystal orientation, to obtain more 1-0-0 plane diamonds. In the prior art, it is typical to first grow CBN to prepare the surface of the substrate for subsequent growth of 1-0-0 plane diamond.

Figure 6B represents a tungsten carbide substrate (602) that has been pre-treated and, as shown therein, the pretreatment process will also result in a desirable rounding off of the peaks of the tungsten carbide grains. In this manner (i.e., by pre-treating the substrate to be surface treated/coated), various advantages accrue. Cobalt can be

WO 95/20253

PCT/US95/00782

minimized or eliminated from the surface, grinding marks and impurities can be removed from the surface, and the structure of the exposed tungsten carbide can be controlled and modified. Generally, by performing such a pre-treatment process, prior to performing the surface treatment (e.g., coating) process, the subsequent surface treatment process can much better be controlled, by imparting known (e.g., constant, repeatable) characteristics to the surface of the substrate being treated. As shown in Figure 6B, a sub-surface region, extending to a depth d' , has been cleared of cobalt. Generally, this is a precursor to the conversion zone described above. Figures 11A and 11B, described hereinbelow, are also descriptive of the pre-treatment process. Additional detail of the process parameters is set forth in the examples described hereinbelow.

In addition to exposing and rounding off the tungsten carbide grains, the pre-treatment process of the present invention effects metallurgical changes within the surface of the substrate. For example (again, in the context of a cobalt-cemented tungsten carbide substrate), diamond having a 1,0,0 crystal orientation can be formed, which will serve as a highly desirable nucleation site for subsequently fabricated diamond (or DLC) coating on the surface of the substrate. Again, this is irrespective of the technique used to coat the substrate, and is useful for CVD processes and the like. However, as will be evident, using the coating fabrication processes of the present invention will result in a synergistic effect, and exponential results, since the same laser equipment is used both to pre-treat (prepare, characterize) and to treat (fabricate a coating on) the substrate. Moreover (again, in the context of a cobalt-cemented tungsten carbide substrate), the pre-treatment process of the present invention advantageously forms a complex of carbon + nitride + cobalt-nitride or prescribed orientation in the valleys between the tungsten carbide peaks which is highly suitable for subsequent coating (or for simultaneous

WO 95/20253

PCT/US95/00782

fabrication of a coating).

SURFACE TREATMENT AND PRE-TREATMENT SYSTEM (FIGURE 7)

An overall process flow (Figure 1), the use of three lasers (Figure 3), introduction of a secondary source (Figures 4, 5, 5A, 5B) and pre-treatment (Figures 6A, 6B) have been described hereinabove.

Figure 7 illustrates a complete surface treatment system 700, suitable for performing the entire repertoire of process steps outlined in Figure 1, utilizing the three laser process described with respect to Figure 3, including introducing one or more secondary sources as discussed with respect to Figure 4, incorporating a preferred nozzle design such as was described with respect to Figures 5A and 5B, and suitable for performing the pretreatment described with respect to Figures 6A and 6B.

The surface treatment system 700 includes three lasers: an ultraviolet excimer laser (LASER 1) 712, an infrared Nd:YAG laser (LASER 2) 714 and an infrared CO₂ laser (LASER 3) 716. Each laser emits a beam which is directed through the opening of the nozzle 722 towards the surface of the substrate 702. The nozzle 722 has an axis 723 which is preferably normal (at 90°) to the surface of the substrate 702. The excimer laser 712 is directed, at a first angle " θ_1 ", towards the surface of the substrate. The Nd:YAG laser 714 is directed, at a second angle " θ_2 ", towards the surface of the substrate. The CO₂ laser 716 is directed, at a third angle " θ_3 ", towards the surface of the substrate. In an exemplary embodiment of the invention, the first angle $\theta_1 = 0^\circ$ (parallel to the axis of the nozzle), the second angle $\theta_2 = -30^\circ$, and the third angle $\theta_3 = +30^\circ$. However, it is within the scope of this invention that the three laser beams can be directed coaxially or in parallel with one another ($\theta_1, \theta_2, \theta_3 = 0^\circ$) through the opening of the nozzle is within the

WO 95/20253

PCT/US95/00782

scope of this invention. The nozzle 722 is disposed at a standoff distance "h" above the surface of the substrate 702.

5 A gaseous secondary source (SS) 720 (e.g., a carbon-containing gas, such as carbon dioxide) is provided through the nozzle 722, and a shielding gas (SG) 724 (a non-reactive or inert gas, such as nitrogen, helium, argon, or the like) is provided thorough the nozzle. Generally, the three laser beams are directed through the nozzle to converge on a selected area of the substrate 702, in the manner discussed hereinabove with respect to Figure 3. However, it is within the scope of this invention that the three laser beams are sized so that each beam completely covers the surface of the substrate (the selected area encompasses the entire surface of the substrate). In this example, the substrate is a rectangular substrate, having dimensions "X" and "Y", and is moved (arrow 732) during surface treatment in the y-axis.

10 In use, with the gases (720, 724) turned on, a plasma (not shown in this figure, see Figure 8) is formed beneath (as viewed) the nozzle, immediately atop the surface of the substrate 702. As mentioned above, the secondary source is converted in the plasma, along with vaporized constituent elements, to fabricate a coating on the surface of the substrate.

25 Generally, the role of the excimer laser 712 is to perform surface ablation, break down the secondary source (SS) and initiate synthesis for bonding and growth (fabrication) of a coating on the surface of the substrate; the Nd:YAG laser 714 assists the excimer laser in breaking down the secondary gas and performs a prominent role in diffusion; and the CO₂ laser 716 helps maintain the thermal balance of the reaction, both in the plasma and on the substrate. With this in mind, although it is preferred that all three laser beams pass through the nozzle,

WO 95/20253

PCT/US95/00782

it is within the scope of this invention that the beam from the CO₂ laser 716 could be directed into the plasma without passing through the opening in the nozzle.

SUBSTRATE SUPPORT AND FLAT PLASMA (FIGURE 8)

5 Figure 8 illustrates apparatus for supporting a substrate 802 being treated, and a preferred shape of the plasma ("PLASMA") being generated in the surface treatment process.

10 A distinct advantage of the present invention is the ability to form a flat plasma that is closely adjacent the surface of the substrate being treated. Moreover, such a flat plasma can wrap around the corners of the substrate, and is advantageous in the fabrication of coatings on round tools such as drills. Generally, the plasma "delivers" secondary elements to the surface of the substrate, and ensures localized (versus) 15 mass heating of the substrate.

20 In this example, the substrate 802 is disposed atop a pedestal 804 which has a button-like projection 808 extending upward from its top (as viewed) surface. The projection 808 is preferably smaller in area than the substrate being supported, and the substrate is disposed concentrically atop the projection. A vacuum passage 810, passing through the pedestal 804 is suitable for "chucking" (holding) the substrate onto the pedestal, and is well suited to automated handling of substrates in a production environment.

25 The plasma shown in Figure 8, created by a surface treatment system such as was described with respect to Figure 7, is a "flat" plasma, in that it is generally coplanar with the surface of the substrate, and is of controlled, minimal, vertical (as viewed) extent. By creating a flat plasma, 30 reactions of vaporized constituent elements (from the substrate)

WO 95/20253

PCT/US95/00782

and secondary elements (from secondary sources) can be well controlled, and localized at the surface of the substrate which is intended to be treated.

5 The flat (squat) plasma shape, and its intimate contact with the surface of the substrate, is advantageous in that it allows for fabrication (growth) of a coating directly on the surface of the substrate. In other words, the flat plasma interacts with the surface of the substrate. This is in marked contrast to CVD systems, and plasmas shaped like tall columns, 10 the coating is "rained" down onto the surface of the substrate. and allows for relatively high coating rates of coating fabrication.

15 A significant advantage of the invention accrues to the flat plasma that can be formed, and vacuum chucking complements the formation of such a flat plasma. Moreover, as illustrated in Figure 8, the plasma generated by the process of the present invention can be caused to wrap around the edges of the substrate being treated. Such wrapping around (the edges of the substrate) of the plasma can be enhanced by providing a 20 plurality of auxiliary vacuum passages 812 through the pedestal, such that these passages exit the top surface of the pedestal outside of the projection 808 yet within the area underneath the substrate. The same (or another) vacuum which serves to hold the substrate onto the pedestal will serve to augment (enhance) 25 wrapping of the plasma around the edge of the substrate.

The reaction mechanisms effected by the combination of lasers and plasma can be classified as "pyrolytic" and "photolytic". Generally, in the pyrolytic mechanism, the laser(s) serve(s) to:

- 30 (a) locally heat the substrate to induce thermal reactions on the surface where it is desired to fabricate a coating,
(b) alternatively, the laser energy is absorbed by the

WO 95/20253

PCT/US95/00782

reactant, which is initially excited into non-dissociative states. After energy relaxation, the reactant gas can dissociate to form thin films,

(c) the substrate and the gas can simultaneously be heated,

5 (d) when the laser directly heats the substrate, gas near the surface is heated and dissociated by diffusion and convection mechanisms.

10 Generally, in the photolytic mechanism (or photochemical process, the laser(s) serve(s) to dissociate gas-phase or surface-adsorbed molecules to form deposit atoms or intermediates without significantly heating the gas or surface of the substrate. Laser excitation could occur by stimulating electronic transitions by the absorption of one ultraviolet photon or, alternatively, by the absorption of several visible
15 or ultraviolet photons. In the latter case, absorption may occur either in a concerted manner, as in multiphoton absorption, or in a sequential manner which may, in fact, involve photon absorption by intermediate products. The photolytic products may further be decomposed by the pyrolytic
20 process.

25 Generally, the output of an excimer laser can effectively be absorbed by carbon dioxide (e.g., from the secondary source), which leads photochemical reactions to break down C-O bonds to form diamond films or reactive intermediates. Since carbon dioxide is essentially transparent to the output of an Nd:YAG laser, the Nd:YAG laser output is mainly absorbed by the reaction intermediate created by the excimer laser, and by the substrate or by some film overlaying it.

WO 95/20253

PCT/US95/00782

EXERCISING CONTROL OVER THE SYSTEM (FIGURE 9)

Figure 9 illustrates, schematically, an overall surface treatment system 900 (similar to the system 700). A substrate 902 is disposed underneath a nozzle (omitted from this view, for illustrative clarity), energy from lasers 910 is directed at the substrate to create a reaction within the surface of the substrate and immediately above the surface of the substrate (including forming a flat plasma), one or more secondary elements are introduced from one or more secondary sources 920 to augment the reaction occurring at the substrate, the substrate can be moved around by a multi-axis positioning mechanism 930 (e.g., a multi-axis robot), and the operation of these components is controlled by a controller 940 (such as a suitably programmed computer). Importantly, the system can exercise control over the timing (e.g., sequence of turning on and off) of the lasers (910), as well as the relationship between pulses delivered by the various lasers.

EXAMPLES

There follows examples of pre-treating a tungsten carbide substrate and fabricating a diamond coating, using a surface treatment such as is described with respect to Figure 7.

In any such process there are, of course, numerous variables, making the process "recipe" different from one substrate type (e.g., material, geometry, size) to another. As aptly noted in the Kabacoff patent (5,176,788), the variables attendant such a process are numerous, complex and interrelated, making a calculations or predictions very difficult. Generally, a better approach is to try different process parameters, within a reasonable range of parameters, observe the results obtained, and empirically optimize the process.

WO 95/20253

PCT/US95/00782

Generally, a system for fabricating a coating on a substrate, according to the present invention, comprises three lasers, each with its own beam delivery system (BDS), employs a nozzle delivering a secondary source (SS) in an envelope of a shielding gas (SG), and creates a flat plasma on the surface of the substrate. More particularly, in the context of fabricating a diamond coating on a tungsten carbide substrate, the substrate may be pre-treated for subsequent coating by any suitable technique for forming a coating on a substrate, including the techniques of the present invention, or an entire surface treatment process may be performed including a pre-treatment regime and a coating regime.

In the examples that follow, a flat carbide cutting tool insert substrate is pre-treated, or is treated (pre-treated and coated) to have a diamond (or DLC) coating. For simplicity, it is assumed that the entire substrate is treated at once (i.e., the beams are of sufficient dimension to "flood" the entire surface area of the substrate). A surface treatment system such as was described with respect to Figures 7 and 9 is employed.

Figure 10 is a process timing diagram illustrating the process of pre-treating a substrate for subsequent fabrication of a coating (or deposition of a coating by a CVD process, or the like).

Figure 10A is a process timing diagram illustrating the process of simultaneously (in-situ) pre-treating a substrate and fabricating the coating.

Figure 11A is a photomicrograph illustrating the surface of a tungsten carbide cutting tool insert (substrate) prior to such pre-treatment, and Figure 11B is a photomicrograph of the

WO 95/20253

PCT/US95/00782

tungsten carbide substrate of **Figure 11A** after pre-treatment. As shown in **Figure 11A** the surface of the substrate is replete with grinding marks and impurities. As shown in **Figure 11B** the surface of the substrate is cleared of grinding marks and impurities, and tungsten carbide grains are exposed amid valleys of cobalt (compare **Figure 6B**).

As shown in **Figure 10**, the pre-treatment process of the present invention involves use of the excimer laser only, and ablated cobalt is suitably removed by the nitrogen shielding gas, which is suitably introduced through the nozzle (550), but which may be introduced across the surface of the substrate by another, simplistic nozzle (not shown).

Figure 10A is a process timing diagram illustrating the orchestration of the lasers and the secondary and shielding gases in a complete surface treatment process including a pre-treatment and a coating fabrication regime.

Generally, as illustrated by **Figure 10A**, three lasers (an excimer laser, an Nd:YAG laser and a CO₂ laser) and two gases (CO₂ as the secondary source, and N₂ as the shielding gas) are operated, in concert, to perform surface treatment in two "regimes" - a pre-treatment regime and a coating regime. **Figure 10** is a diagram illustrating the time at which each of these components is turned on and turned off. The numbers on the timing diagram (e.g., "0", "12", "25", etc.) represent seconds.

As discussed with respect to **Figures 6A and 6B**, the surface treatment system of the present invention is suitably employed to perform pre-treatment of the substrate.

Figure 10 illustrates a pre-treatment regime lasting approximately twenty seconds, in a time interval between "p0" and "p1", wherein the substrate is pre-treated by the excimer

WO 95/20253

PCT/US95/00782

laser (e.g., 712) only, to prepare the surface of the substrate for further treatment.

As shown in Figure 10, during the pretreatment phase, the nitrogen (shielding) gas is also turned on to convey ablated material (cobalt, oxides) away from the substrate. Preferably, the nitrogen is left on for a brief interval (from "p1" to "p2") after the excimer laser is turned off to ensure that the ablated material is completely removed from the surface of the substrate.

The surface treatment technique may be performed, combining pre-treatment and coating fabrication, as illustrated by Figure 10A. Therein, at a time "t0" the surface treatment commences. During the entire surface treatment process, extending from time "t0" to time "t5", the excimer laser (e.g., 712), the secondary source (e.g., 720) and the shielding gas (e.g., 724) are turned on.

The excimer laser is operated during the entire surface treatment process ("t0" through "t5"), generally according to the parameters set forth above. However, the output of the excimer laser may be modified "on the fly" during the coating regime, notably to initiate pre-treatment (in the interval between "t0" and "t1"), and to take up "slack" from the Nd:YAG laser which may be turned off at time "t3" (discussed hereinbelow). During the surface treatment process, the excimer laser is suitably operated at 450 mJ at a pulse frequency of 280 Hz.

As illustrated by Figure 10A, it is not necessary to turn the Nd:YAG laser (e.g., 714) on immediately at "t0". Rather, its debut into the process (coating regime) can be delayed for a brief interval of time (e.g., for 5 seconds). Generally, during this excimer-only interval ("t0" to "t1"), a leading edge

WO 95/20253

PCT/US95/00782

zone of a substrate can be pre-treated (see, e.g., Figure 12B). Similarly, it is not necessary that the Nd:YAG laser participate during the entire coating regime, and it may make an early exit at time "t3", approximately 10 (e.g., 12) seconds prior to
5 turning off the excimer laser.

Similarly, as illustrated by Figure 10A, it is not necessary to turn on the CO₂ (e.g., 716) on immediately at "t0". Rather, its debut into the process can be delayed for a brief interval of time (e.g., for 12 seconds"). Similarly, it is not
10 necessary that the CO₂ laser participate during the entire treatment phase, and it may make an early exit at time "t4", approximately 5 seconds prior to turning off the excimer laser.

More particularly:

1. First Laser: The excimer laser plays a principal role
15 in surface ablation and breaking chemical bonds in the secondary source (e.g., CO₂), and has the following beam delivery parameters:

- a. wavelength 192nm, 248 nm or 308 nm (nanometers), in the ultraviolet range of wavelengths, preferably 248 nm;
- 20 b. power output up to 200 W (watts), preferably 100 W (A lower power, such as 75 W can be employed for round tools);
- c. pulse energy up to 500 mJ (millijoules), preferably 450 mJ;
- d. pulse sequence frequency (repetition rate) up to 300 Hz
25 (Hertz), preferably 280 Hz;
- e. energy density of up to 30 mJ/mm², preferably 25 mJ/mm²;
- f. pulse length (duration) up to 26 ns (nanoseconds), preferably 18 ns;
- g. beam profile - rectangular; and
- 30 h. divergence - 3.5 milliradians (mrad).

The beam delivery system (BDS) for the excimer laser

WO 95/20253

PCT/US95/00782

includes a rectangular lens to deliver a rectangular beam (focused) having dimensions 1 mm x $\frac{1}{2}$ inch, and the lens is disposed about 18 inches upstream (towards the laser) from the nozzle aligned with the nozzle axis.

5 To perform pretreatment only (e.g., Figure 6B), the excimer laser is on for 20 seconds at 350-380 mJ, pulsed at a frequency of 220-250 Hz, at 100 watts, and performs surface ablation (removing surface marks and impurities, removing cobalt from a surface region of the substrate).

10 To perform a complete surface treatment (i.e., integrating pre-treatment and coating regimes), the excimer is on for 45 seconds at 450 mJ, pulsed at a frequency of 280 Hz, at 100 watts, and (i) reacts and breaks bonds in the secondary source (CO_2), and (ii) initiates synthesis for bonding and growth.

15 2. Second Laser: The Nd:YAG laser, which plays a principal role in the diffusion function suitably has the following beam delivery parameters:

- a. wavelength 1.06 microns (E-6 seconds), in the infrared range of wavelengths;
- 20 b. power output up to 1500 Watts (W), preferably 1000 W;
- c. pulse energy up to 150 Joules (J), preferably 50 J;
- d. pulse sequence frequency, continuous wave (CW), burst mode, or Q-switch up to 1000 Hz (Hertz), preferably 120 Hz;
- e. pulse length (duration) up to 20 ms (milliseconds),
- 25 preferably 1 ms;
- f. beam profile - round; and
- g. divergence 55 mrad.

The beam delivery system (BDS) for the Nd:YAG laser includes a circular lens to deliver a circular beam (diffused)

30 having a radius of $\frac{1}{2}$ inch, and the lens is disposed about 18 inches upstream (towards the laser) from the nozzle at an angle

WO 95/20253

PCT/US95/00782

of approximately -30° (30° in a one direction) from the nozzle axis.

In a pre-treatment only regime, the Nd:YAG laser is not operated.

5 In an integrated surface treatment process, including pre-treatment and coating regimes, the Nd:YAG laser is on for at least a portion (e.g., "t1" to "t3", see Figure 10A) of the process. The Nd:YAG laser is turned on 5 seconds after the
10 excimer laser is turned on, for 35 seconds, pulsed at a frequency of 120 Hz, at 1000 watts, to (i) assist the excimer laser in breaking the bonds in the secondary source (CO_2), and to perform a primary (or sole) role in diffusion bonding.

15 3. Third Laser: The CO_2 laser, which plays a principal role in the supporting thermal balance, suitably has the following beam delivery parameters:

- a. wavelength 10.6 microns, in the infrared range of wavelengths;
- b. power output on the order of 500 - 10,000 Watts (W), preferably 2000 W.
- 20 c. pulse sequence frequency up to 25 Hz, pulse up to 25 microseconds; super-pulse frequency up to 20 KHz (KiloHertz), and a super-pulse width up to 500 microseconds;
- d. energy density up to 0.32 J/cm^2 ;
- e. beam profile - round;
- 25 f. divergence - $1\frac{1}{2} \text{ mm/m}$; and
- g. in a pulse stream mode, a pulse stream duration of up to 5 seconds.

30 The beam delivery system (BDS) for the CO_2 laser includes a circular lens to deliver a circular beam (diffused) having a radius of $\frac{1}{2}$ inch, and the lens is disposed about 18 inches upstream (towards the laser) from the nozzle at an angle of

WO 95/20253

PCT/US95/00782

approximately +30° (30° in a direction opposite the direction of the Nd:YAG laser) from the nozzle axis.

In a pre-treatment only regime, the CO₂ laser is not operated.

5 In the integrated pre-treatment and coating process, the CO₂ laser is turned on approximately 12 seconds ("t₂") after the excimer laser is turned on, for a duration of 28 seconds, pulsed at a super-pulse frequency of 1.5 kHz, at 2000 watts, to (i) maintain thermal balance during the process (synergy between the
10 surface reaction and the gas reaction) (ii) change of absorption rate changes during the process (iii) control the substrate temperature at the order of 1 ns (nanosecond). The CO₂ laser may be turned off shortly prior to the end of the process (e.g., at time "t₄").

15 Generally, the pulsations of the excimer and Nd:YAG lasers work together to "hammer" (create a shock wave, stress, and relax) the at the components of the plasma, dissociating same, inter alia. To this end, the phase relationship between the pulses delivered by these two lasers are preferably adjusted
20 (coordinated) to optimize the concerted hammering, depending upon the particular application of the system. These parameters are, at best, empirically determined.

25 4. Beam Delivery System: The beam delivery system (BDS) conveys the laser beams to a surface treatment "cell" (area for performing surface treatment), establishes the cross-section and focus of the beams, includes the lenses described hereinabove for each of the three lasers. Suitable, the excimer beam is delivered as a rectangular (cross-section) beam, and the beams from the Nd:YAG and CO₂ lasers are delivered as circular (cross-
30 section) beams.

WO 95/20253

PCT/US95/00782

5. Shielding Gas: The shielding (inert) gas (SG), which isolates the secondary element (SS) from the ambient environment (e.g., air) is suitably nitrogen (N_2), delivered by the nozzle (e.g., 550) in gaseous form.

5 During a pre-treatment only regime, the nitrogen gas is introduced during the pretreatment period (0-20 seconds) at a flow rate of 40 sccm. The nitrogen gas removes the ablated cobalt or oxides. At the termination of the pretreatment regime, the nitrogen gas remains flowing for a few additional
10 seconds to ensure that undesired (e.g., ablated) elements are completely flushed (directed) away from the surface of the substrate.

15 During an integrated surface treatment process, the nitrogen gas is introduced during the entire treatment period (e.g., 45 seconds, while the excimer laser is turned on), at a flow rate of 25 sccm. During the process, the nitrogen gas stabilizes and shields (i.e., from the ambient atmosphere) the process. Generally, the purpose of the shielding gas (e.g.,
20 nitrogen) is to prevent formation of residual oxides (from combination with atmospheric oxygen). The nitrogen shielding gas serves to (1) prevent formation of oxides, (2) direct ablated cobalt and/or tungsten carbide away from the surface, and (3) if desired, form nitrides (e.g., carbon nitride or cobalt nitride) for fabricating preferred diamond crystal
25 orientation in the 1,0,0 plane (see, e.g., Figure 11F).

6. Secondary Element: The carbon-containing secondary source gas (SS) is preferably CO_2 , delivered by the nozzle in gaseous form. Other carbon-containing gases could be used, but are generally either toxic (e.g., CO) or flammable (e.g.,
30 methane).

WO 95/20253

PCT/US95/00782

During a pre-treatment only regime, it is not necessary to introduce the carbon dioxide gas, since a secondary source is not required.

5 During a comprehensive surface treatment process, the carbon dioxide gas is introduced during the entire treatment period (e.g., 45 seconds, while the excimer laser is turned on), at a flow rate of 60 sccm. During the process, the carbon dioxide gas is broken down (by the lasers) into carbon elements serving as secondary elements augmenting formation of the
10 coating.

7. Nozzle: The nozzle is ring-shaped, has a plurality of passages disposed about its inner diameter, and is located approximately 6 inches above the surface of the substrate. This standoff distance "h" is selected to allow for dissociation and
15 reaction of the secondary element prior to diffusion into the substrate and/or fabrication of the coating on the surface of the substrate.

8. Substrate: The substrate is a tungsten carbide, rectangular, cutting tool insert, measuring $\frac{1}{2}$ inch by $\frac{1}{2}$ inch.
20 Such a substrate may contain 94% tungsten carbide (W_2C) with 6% cobalt (Co) binders. Cobalt has a tendency to migrate to the surface, which is not desirable for fabricating a diamond (or diamond-like carbon) coating. The objective is to remove cobalt from the surface (and subsurface region), and this is done with
25 the excimer laser in the pre-treatment regime, taking advantage of the fact that cobalt evaporates faster than tungsten carbide. After pre-treatment, tungsten carbide crystals (grains) are exposed at the surface of the substrate and, beneath the surface, the tungsten carbide crystals combine with neighboring
30 Co binders to form a desirable W_2C -Co element. The tungsten carbide at the surface and the tungsten-carbide-cobalt element below the surface provides desirable nucleation sites for

WO 95/20253

PCT/US95/00782

subsequent diamond growth (during the coating regime).

The surface treatment process was performed on an "of-the-shelf" Kennametal (Latrobe, PA) "K68" grade cutting tool insert, having 92% WC, 2% Ta(Nb)C, and 6% Co, a fine grain size, a transverse rupture strength of 2000 N/mm² (Newtons per millimeter squared), a density of 14.9 g/cm³ (grams per centimeter cubed), and an HRA hardness of 92.7.

The surface treatment process is also suitable, for example, for an "off-the-shelf" Kennametal (Latrobe, PA) "K313" grade cutting tool insert, having 93.5% WC, 0.5% Cr₃C₂, and 6% Co, an average grain size of 1 μm (micron), a transverse rupture strength of 3000 N/mm² (Newtons per millimeter squared), a density of 14.9 g/cm³ (grams per centimeter cubed), and an HRA hardness of 93.0.

Generally, the integrated surface treatment process of this invention is suitable for any "off-the-shelf" substrate, without requiring modifying (e.g., grinding, etching, etc.) the substrate prior to treatment.

9. Plasma Plume: The plasma plume exhibits an oblique shape surrounding a cross-section of the substrate, and the substrate is preferably traversed through the plume to coat the desired area (e.g., entire "top" surface) of the substrate.

Figure 10B is a graph of beam power (P(W), vertical axis) versus pulse frequency (f(Hz), horizontal axis) for the excimer laser, operating at three (of several) different power levels (100 W; 87.5 W; 75W). As noted above, a power of 100 W is suitable for treating flat cutting tool inserts, and a power of 75 W is suitable for treating round cutting tools.

WO 95/20253

PCT/US95/00782

Figure 10C is a tabular listing of program data for the Nd:YAG laser. Each program number (1-13) has set of corresponding pulse frequency, burst time, pump pulse energy and maximum frequency.

5 Figure 10D is a detailed power (vertical axis) versus time (horizontal axis) profile for the CO₂ laser, corresponding to the generalized parameters described with respect to Figure 10A.

With reference to these Figures 10B, 10C and 10D:

10 (a) for surface treating a flat cutting tool insert, the excimer laser is operated with an output power of 100 W (Watts), with a pulse duration of 400 ms (milliseconds), in conjunction with the Nd: YAG laser operating according to PROGRAM NUMBER 4 on the table of Figure 10C and the CO₂ laser operating according to the profile of Figure 10D;

15 (b) for surface treating a flat tool insert, the excimer laser may also be operated with an output power of 87.5 W (Watts), with a pulse duration of 350 ms (milliseconds), in conjunction with the Nd: YAG laser operating according to PROGRAM NUMBER 11 on the table of Figure 10C and the CO₂ laser operating according to the profile of Figure 10D; and

20 (c) for surface treating a round tool insert (as discussed below with respect to Figure 16A), the excimer laser is operated with an output power of 75 W (Watts), with a pulse duration of 300 ms (milliseconds), in conjunction with the Nd: YAG laser operating according to program number (Program No.) 11 on the table of Figure 10C and the CO₂ laser operating according to the profile of Figure 10D.

WO 95/20253

PCT/US95/00782

PHOTOMICROGRAPHS AND RAMAN ANALYSIS

The photomicrographs and Raman analysis of **Figures 11A, 11B, 11C, 11D and 11E** relate to the example of fabricating a diamond coating on a tungsten carbide substrate, set forth above.

Figure 11A is a top view photomicrograph of the specimen (Prior Art) prior to surface treatment. As shown therein, an off-the-shelf cutting tool insert will exhibit a pattern of grinding marks (evident as oblique lines in the figure) and may also have contaminants on the surface (evident as specks in the figure). As indicated above, it is preferable to perform pre-treatment to characterize the surface of the substrate prior to coating, in addition to ablating cobalt and exposing tungsten carbide grains. **Figure 11A**, although related to **Figure 6A**, shows in greater detail some of the challenges inherent in surface treating existing substrates.

Figure 11B is a top view photomicrograph of the specimen of **Figure 11A** after pre-treatment, according to the present invention. As shown therein, there are a plurality of tungsten carbide "hills" 1134 (corresponding to 634 in **Figure 6B**) surrounded by cobalt "valleys" 1132 (corresponding to 632 in **Figure 6B**). In this manner, the surface of the substrate is pre-characterized for subsequent coating, the tungsten carbide hills serving as defined nucleation sites for subsequent growth of diamond (or DLC).

Figure 11C is a top view photomicrograph of the specimen after coating, according to the present invention. As shown illustrated therein, a plurality of substantially uniform diamond crystals (the exposed portions of which appear as pyramid-like structures in the figure) have been formed on the surface of the substrate.

WO 95/20253

PCT/US95/00782

Figure 11D is a Raman spectrograph taken of the treated specimen. The vertical axis is absorption, and the horizontal axis is wave number. As is evident therein, there is a sharp (narrow) peak at 1332 cm^{-1} . This provides evidence that the coating contains carbon in the sp^2 crystalline phase, as well as a noticeable amount of diamond-like carbon. As discussed hereinabove, such analysis is merely indicative, and is not dispositive of the "quality" of the coating - actual cutting tests should be performed to make such a determination.

Figure 11E is a side view (cross-sectional) photomicrograph representation of the specimen after coating, according to the present invention. As shown therein, a transition zone 1150 extends from the surface of the substrate to a depth "d" into the substrate 1152, and a diamond (or DLC) coating 1154 having a thickness "t" is evident on the surface of the substrate. In a specimen that was surface treated according to the present invention, the depth of the transition zone was observed to be $10\text{ }\mu\text{m}$ (microns), and the thickness of the diamond (or DLC) coating was observed to be $45\text{ }\mu\text{m}$. With 45 seconds of coating regime, this confirms a coating growth rate on the order of $1\text{ }\mu\text{m/s}$ (micron per second).

A "telltale" sign that the surface treatment process of the present invention was performed on a substrate are the sporadic traces (artifacts) 1156 of complex carbides (e.g., with respect to treating a tungsten-carbide cutting tool insert), carbon nitrides, and the like, readily evident in the transition (diffusion) zone 1150 of the substrate. This zone 1150 can also be termed a "differential compositional layer". These "roots" (of the coating), or an analogous feature (depending on the coating material being fabricated and the material of the underlying substrate) would be evident in virtually any product (substrate) treated by the surface treatment process of the

WO 95/20253

PCT/US95/00782

present invention and would serve as an artifact to distinguish (evidence) products made by the process of the present invention from products made by other (e.g., CVD) processes, especially if the substrate is a tungsten carbide substrate having a diamond or diamond-like carbon coating.

Among the many advantages of the present invention is that no "seeding" is required to fabricate a diamond coating on a substrate. Due to the nature of localized heating, overall (mass) substrate temperatures can be maintained as low as 30°C.

SCANNING ACROSS A SUBSTRATE

As mentioned above, the surface treatment system of the present invention is suited to treating selected areas (rather than the entire surface, at once) of a substrate. In general, this is a function of the profile (cross-section) of the laser beams. By suitable sizing and shaping of the beams, the selected area can span an entire "zone" across the surface of the substrate, and the substrate can be advanced during treatment so that the entire surface of the substrate is treated.

As noted hereinabove, the beams from the three lasers may be converged on a selected area of a substrate being treated, and the beams are delivered (generally through a gas nozzle) to the substrate via respective beam delivery systems (see, e.g., elements 322, 324 and 326 of Figure 3). It has been determined, that the process can be optimized by controlling the profile of the individual beams.

Figure 12A illustrates the beams from three lasers converging on the surface of a substrate 1202. Generally, the cross-sections of the beams are selected and controlled with regard to the dimensions of the substrate being treated. In

WO 95/20253

PCT/US95/00782

this example, a rectangular substrate 1202 having dimensions "X" and "Y" is undergoing treatment (nozzle omitted, for illustrative clarity), and is being moved along its y-axis, as indicated by the arrow 1232 (compare 332, 432).

5 The excimer laser (e.g., 712) is caused by a rectangular lens 1252 to have a rectangular (cross-section, profile) beam 1262 of dimensions "a" and "b", wherein the dimension "a" of the beam is generally aligned with the transverse dimension "X" of the substrate, and the dimension "b" of the beam is generally
10 aligned with the longitudinal dimension "Y" of the substrate. Generally, the dimension "a" is larger than, and subsumes the dimension "X" to ensure that the beam will completely cover a rectangular section (from one side edge 1202c to an opposite side edge 1202d) of the substrate. By causing the substrate to
15 move, relative to the beam (as indicated by the arrow 780), the excimer beam will traverse (in the "y" direction) the entire surface of the substrate 1202, from a "leading" edge 1202a of the substrate 1202 to a trailing edge 1202b of the substrate 1202. A beam having such a cross-section would generally be
20 considered to be a focused beam.

 The Nd:YAG (e.g., 714) and CO₂ (e.g., 716) lasers are caused, by spherical lenses 1254 and 1256, respectively, to have circular cross-section beams 1264 and 1266, respectively, impinging on the surface of the substrate at angles θ_2 and θ_3 ,
25 respectively (compare Figure 7). The two beams 1264 and 1266 may have similar circular cross-sections of radius "r" although, as shown, they are introduced towards the substrate from opposite sides of the excimer beam 1262. Preferably, the radii "r" of these two beams 1264 and 1266 are greater than the
30 largest (transverse dimension "X" or longitudinal dimension "Y") dimension of the substrate.

WO 95/20253

PCT/US95/00782

In Figure 12A, the beams 1262, 1264, 1266 are illustrated as dashed lines, and the resulting pattern of three beams converging on the surface of the substrate is shown by the dashed line 1270. This pattern 1270 of beam convergence would, in practice, be on the surface of the substrate, and comprises three portions: (1) a first, generally semicircular portion 1270a comprising the convergence of the beams from the Nd:YAG and CO₂ lasers; (2) a second, generally semicircular portion 1270b comprising the convergence of the beams from the Nd:YAG and CO₂ lasers; and (3) a third, generally rectangular portion 1270c disposed between the first 1270a and second 1270b portions.

Beam profiles, such as those discussed with respect to Figure 12A were employed in the experiment described above with respect to coating a tungsten carbide cutting tool insert.

Figure 12B illustrates the substrate 1202 (in cross-section) moving (arrow 1210) under the pattern of beam convergence 1270 (shown in perspective). As the substrate is advanced (moved) under the beams, the substrate is progressively surface treated, from its leading edge 1202a to its trailing edge 1202b, as illustrated by a coating 1204 and a conversion zone 1206 in a selected area extending from (and partially over) the leading edge 1202a of the substrate 1202 towards the trailing edge 1202b of the substrate 1202. Such a process was successfully employed to fabricate a diamond coating on a tungsten carbide substrate, according to the process parameters set forth hereinabove.

TAILORED COATINGS (FIGURES 13A - 13H)

The technique of the present invention is useful for fabricating a variety of coatings on a variety of substrates.

WO 95/20253

PCT/US95/00782

For example, as discussed with respect to Figure 2B, multi-layer coatings can be fabricated on the surface of a substrate. In the figures that follow, numerous exemplary applications of the technology and products produced by the technology are described. As discussed above, selected areas of a substrate can selectively be surface treated. According to an aspect of the invention, the surface treatment technique of the present invention is suitable for fabricating "tailored" coatings on a substrate.

Figure 13A illustrates a substrate 1302 having four surfaces 1304, 1306, 1308 and 1310 which can be distinctively treated according to the techniques of the present invention. A coating 1314 is fabricated on the surface 1304, a coating 1316 is fabricated on the surface 1306, a coating having two segments (1318a and 1318b) is fabricated on the surface 1308, and a coating 1320 is fabricated on the surface 1310. Assuming that the beam (not shown) is always incident from the top (as viewed), the substrate will need to be moved (e.g., scanned in the x-y plane) in order for the beam to treat a substantial area of the surface 1304. As shown, the coating 1314 covers less than the entire area of the surface 1304, and more area than one reaction zone. It is also evident that the substrate will need to be rotated in order to treat the side surfaces 1306 and 1310 which are parallel to the beam 1312, and the opposite surface 1308 which is entirely blocked from the beam. By rotating these surfaces into position, they may be treated with the same ease as treating the surface 1304. As illustrated in the figure, each of the coatings (and segments) may be of a different thickness and extent (area coverage) than the other of the coatings. Each coating (and segment) may also be of different composition than the other coatings, depending on the selection of secondary element introduced to the reaction system during the formation of the coating. Primary conversion zones and secondary conversion zones (not shown, for illustrative

WO 95/20253

PCT/US95/00782

clarity) below the surface of the substrate may also differ from surface-to-surface, depending on the process parameters invoked during the treatment of the particular surface of the substrate.

Figure 13B illustrates a feature of the invention wherein different thickness regions of a coating and/or different coating layers each having a different area coverage can be fabricated on the surface of a substrate 1322. (Primary and secondary conversion zones are omitted from this figure, for illustrative clarity.) In this example, a first coating 1324 is fabricated on a surface 1326. A second coating 1330 is fabricated over a top surface 1328 of the first coating 1324, and is of lesser extent (area coverage) than the first coating 1324. The coatings 1324 and 1330 can be of similar or dissimilar composition, and of similar or dissimilar thickness.

According to a feature of the invention, the energy (e.g., from three lasers) driving the reaction system may be directed at selected areas of the substrate, and can be scanned in any pattern on the surface of the substrate, to fabricate any desired "profile" (e.g., compositions, thickness, shape) or pattern of coatings on the substrate.

Figure 13C shows a substrate 1350 having a "tailored" coating fabricated on its surface. (Primary conversion zones and secondary conversion zones are omitted, for illustrative clarity.) Portions 1338 of the coating are flat. Other portions 1340, 1342, 1344 are of limited extent (area coverage), and are fabricated to be thicker than the portions 1338 so that they extend above (higher than) the portions 1338. Further, the portions 1340, 1342, 1344 can be formed to be tapered (1340), to have a flat top surface (1340, 1344), to have steep sidewalls (1340, 1344), to be rounded (1342, 1344), to have a convex top surface (1342) or to have a concave top surface (1344). Each portion of the coating illustrated in Figure 13C may be caused

WO 95/20253

PCT/US95/00782

to be of different composition (e.g., by using different secondary sources for each portion of the coating).

This illustrates only a few of the complex coating shapes that can be fabricated using the techniques of the present invention. For example, chip-breaker geometry can be fabricated on a flat cutting tool insert as an integral part of the coating. As a corollary to this, the coating technique of the present invention is applicable to fabricating coatings having uniform thickness on substrate surfaces having irregular topology (such as would be the case (e.g.) with a cutting tool insert substrate having chip-breaker features incorporated into the substrate itself).

Figure 13D illustrates an additional "menagerie" of shapes that can be fabricated as coating structures on the surface of a substrate, including cylinders 1352, tubular structures 1354, conical structures 1356, "L"-shaped structures 1358, curved structures 1360, and tower-type structures 1362. The tower-type structure 1362 is demonstrative of a particularly remarkable feature of the present invention, namely its true heteroepitaxial (omnidirectional) capabilities. In order to form such a coating structure, the base portion 1362a of the structure is first fabricated to extend away from the surface of the substrate, then the substrate (or the energy source/secondary source) is re-oriented, and growth of the structure is continued in another (orthogonal, as shown) direction to form the segment 1362b. Another remarkable feature of the present invention is that all of the structures shown in this figure can be fabricated on the same surface of the same substrate, and each structure can have a composition differing from the other structures. By way of analogy, the substrate can be viewed as a countertop, upon which any number of useful objects can be placed. (Of course, these objects will be diffusion bonded to the countertop using the techniques of the

WO 95/20253

PCT/US95/00782

present invention.) For example, a flat planar cutting tool insert could be coated to not only have a diamond coating, but so that the diamond coating is tailored to have its own chip-breaking geometry (structure).

5 **Figure 13E** illustrates another remarkable, and useful, feature of the present invention. In this case, a snake-like coating 1366 is formed on a surface of a substrate 1368 (compare 1360, Figure 13D). In this case, it is desired to form different coating compositions in different segments of the
10 snake. For example, a first segment 1366a can be fabricated to have a first composition, a second segment 1366b can be fabricated to have a second composition, a third segment 1366c can be fabricated to have a third composition, and a fourth segment 1366d can be fabricated to have a fourth composition.
15 The remaining segments can be fabricated to repeat the sequence (first, second, third, fourth compositions). Alternatively, the segments can represent a code, analogous to storing information (binary, trinary, quinary, etc) in the snake. These techniques are, for example, analogous to forming a diamond (e.g.)
20 chromosome. The resolution (size) of the segments is limited only by the wavelength of the lasers employed to form the segments, and segments having lateral dimensions on the order of 308 nm are readily formed. A "snake" of titanium-carbide, vanadium, and chromium-nitride could readily be formed. The
25 individual segment can be alternatively magnetic and non-magnetic, semi-conductive and non-conductive.

Figure 13F illustrates how a number (nine shown) of coating segments (1372a .. 1372i) can be formed in an array on a surface of a substrate 1370. Each of the segments of the array can be
30 formed of a different composition, and each of the segments can be formed of a different thickness. The segment 1372b is shown having a greater thickness than the remaining segments (1372a, 1372c .. 1372i). Any, or all, or the segments can also be

WO 95/20253

PCT/US95/00782

fabricated as a multi-layer structure (compare Figure 2B).

Figures 13A-10F illustrate the capability of the techniques of the present invention for fabricating "designer" coatings and compositions, by utilizing the techniques of the present invention.

Figures 13G and 13H illustrate techniques for treating cylindrical objects, as exemplary of the ability of the present invention to coat surfaces that are not flat. Coating can punches would be a useful application of such techniques.

In Figure 13G, a cylindrical coating 1380 is fabricated on a cylindrical substrate 1382. The cylindrical substrate may be of any length. This illustrates the continuous nature of the technique of the present invention. For example, the cylindrical substrate may be a wire (e.g., copper) of extraordinary length (thousands of feet). By passing the wire through a workstation, the coating reaction can be performed continuously along the length of the wire.

In Figure 13H, it is illustrated how bands 1384a and 1384b of coatings can be applied at different longitudinal positions along a cylindrical substrate, such as a wire. These bands, of course, could be segments and may be magnetic or nonmagnetic or other properties to differentiate one segment from the other (compare the snake 1366 of Figure 13E).

RAPID PROTOTYPING (FIGURE 13I)

Figure 13I illustrates, generally, the truly heteroepitaxial nature of the invention. The fabrication of coatings is commenced on one or more (one shown) selected areas of the surface of a substrate 1390. As will be evident, the substrate may be a "sacrificial" substrate, which can be excised

WO 95/20253

PCT/US95/00782

from the resulting built up (fabricated) coating structure(s).

5 An exemplary coating structure 1392 is shown as being fabricated (built-up) from a selected area of the surface of the substrate 1390. This can be considered to be growth in a z-axis (normal to the surface of the substrate).

10 By way of example, a portion 1392a of the coating surface 1392 is built-up in the Z-axis to a level "t1", above the surface of the substrate, at which point the substrate (or treatment source(s) can be re-oriented (e.g., with respect to the energy source and the secondary source) so that another portion 1392b of the coating structure 1392 can further be grown (fabricated) in a different direction (e.g., parallel to and spaced apart from the substrate, as shown). The growth of the portion 1392b can be considered to be an X-axis direction. The
15 fabrication of this portion 1392b of the structure proceeds to any desired extent.

20 Likewise, it is possible to re-orient the substrate (or treatment source(s)) so that growth of the structure 1392 proceeds in a different direction from any point along the portion 1392b. This is illustrated by a portion 1392c of the structure being fabricated in what can be considered to be growth in a Y-axis.

25 Evidently, the shape (outline and area) of the fabricated structure 1392 is different between the surface of the substrate and a level t2 than it is between the levels t2 and t1.

30 This demonstrates, in a very generalized manner, the truly heteroepitaxial (omni-directional) nature of the invention, namely that coatings (and coating structures, and portions thereof) can be performed in any direction (e.g., in any of the X, Y and Z axis). The figure is intended to demonstrate that

WO 95/20253

PCT/US95/00782

a coating structure having a distinct outline at any given level (e.g., above the surface of the substrate) can be fabricated. The outline at any of these given levels is not constrained by the outline of the previous level. Further, the area coverage of the structure at any given level is not constrained by the area coverage (e.g., "footprint") of the previous level. At any given level (height) above the surface of the substrate, any outline or area coating structure can be fabricated, and control over the fabrication is suitably effected simply by taking appropriate cross-sections from a computer-generated representation of the object sought to be fabricated as a growth structure, for example. In this manner, a three-dimensional structure of unconstrained shape or form can be fabricated on a substrate. After fabricating the three-dimensional structure, the substrate may be cut off and discarded, or dissolved away, or removed by any means including mechanical or chemical means.

The process of the present invention may be combined with an apparatus controlled by a Computer Numerical Control (CNC) system which accepts stereolithographic software files (e.g., .StL) to facilitate fabrication of objects having complex parts. These objects may be formed from simple, flat, or cylindrical substrates which are manipulated in a fashion to fabricate (e.g., prototype) products using the methods set forth in this invention.

Thus, the apparatus and method according to the present invention can be used to produce complex prototype parts of composite materials to finished workpiece dimensions from CAD data. Furthermore, metal, ceramic, and composite parts can be produced to a final state, requiring no post-process finishing and exhibiting enhanced physical properties by virtue of advanced material compositions not capable of being produced by prior art methods.

WO 95/20253

PCT/US95/00782

TUBULAR SUBSTRATES (FIGURES 14A and 14B)

The techniques of the present invention are useful for coating the inner diameters (ID) of tubular substrates, and are especially useful for coating the ID of tubes having a large ratio of length (L) to diameter (D) (greater than 3:1).

Figure 14A illustrates one technique for coating the inside diameter (ID) of a tubular substrate 1402. An energy beam 1404 (e.g., from three lasers) is directed into one (open) end 1406 of the tubular substrate 1402. The other end 1408 of the tubular substrate is closed off, preferably by concave (or may be convex, not shown) parabolic reflecting surface 1410 (shown spaced apart from the end 1408, for illustrative clarity). In this manner, the beam 1404 will bounce around inside of the tubular substrate, and treat the entire ID of the tubular substrate. A secondary element may or may not be introduced into the system, as desired.

Figure 14B illustrates another technique for coating the ID of a tubular substrate 1412. An energy beam 1414 (compare 304, Figure 3) is directed into one (open) end 1416 of the tubular substrate 1402. The other end 1418 of the tubular substrate may also be left open. A secondary element may also be introduced, as indicated by the stream 1420 (e.g., of gaseous secondary element).

For tubular substrates having exceptional depth (e.g., high L:D), it is possible to dispose a simple (e.g., flat) reflecting mirror within the ID of the tubular substrate to direct the incident energy beam to selected areas on the ID of the tubular substrate. In this manner, selected areas (axial, circumferential, helical) of the ID can be treated by the beam. Further, by sequencing the introduction of a secondary source, the treatment can be varied from selected area to selected area,

WO 95/20253

PCT/US95/00782

in a manner similar to that of Figures 13E, 13F and 13H).

The present invention is useful for coating any of a number of substrates, several of which have been discussed hereinabove. For example, the inner or outer diameters of a helical travelling wave tube could be treated and/or coated, as well as to produce windows for traveling wave tubes. Resistive heating elements could be treated and/or coated, for example, to aid in heat distribution, as well as the inner and/or outer surfaces of cookware. Coatings can be fabricated on replacement hip joints, and the like, so that a portion of the object being coated is provided with a low-friction coating (with, if required, enhanced high load-carrying capacity), while another portion of the object is provided with a porous or textured coating (e.g., to promote bonding to a bone surface). Gun barrels, cylinder liners, and the like, can advantageously be treated by the techniques of the present invention. Razors, knives and scalpels can easily have their cutting edges treated by the techniques of the present invention. Cutting tools, such as drill bits, can be improved by fabricating stepped flutes, by fabricating a diamond coating on the flank of the tool, and by fabricating chip-breaker geometry into the tool, which would otherwise be difficult to achieve using grinding apparatus. Diamond, for example, is soluble with iron, in which case it may be desired to form a silicon nitride coating on the tool (or other substrate). The present invention is capable of extracting and forming a composite material with virtually any constituent (primary) element from a substrate and secondary element, including silicon, copper, oxygen, nitrogen, boron, and the like. The application of the techniques of the present invention to dry machining are virtually unlimited.

COATING WEAR SURFACES (FIGURES 15A and 15B)

Figure 15A shows a component 1552 of a ball bearing, which

WO 95/20253

PCT/US95/00782

has had the surface of its race treated to have a hard (e.g., diamond or DLC) coating 1554. This, for example, will allow for the bearing to function without (or with less) lubrication, in much the same manner as treating machine tools according to the present invention facilitates dry-machining.

Figure 15B shows a component 1562 of a ball bearing, which has had the entire surface of the component 1562 treated to have hard (e.g., diamond or DLC) coating 1566. In this manner, the coating 1566 will function as a heat sink, so as to remove heat from the ball and race, and for protecting against corrosion.

COATING ROUND TOOLS (FIGURES 16A - 16D)

Figure 16A illustrates one embodiment 1600 of coating a round tool (e.g., an end mill, a drill, or the like). An end mill 1602, having a shaft portion 1604, a fluted portion 1606 and a tip 1608 is aligned, as shown, with its tip facing upward towards lasers and a nozzle (not shown). In the manner described hereinabove, a plasma 1610 is generated in the vicinity of the tip. The plasma 1610 will "wind" its way down the flutes of the end mill, resulting in a coating being fabricated along the entire length of the fluted portion 1606. Generally, as will be evident, this embodiment is preferred for forming a thin film diamond (or DLC) coating along the length of the fluted portion. In this embodiment, a vacuum chuck, similar to the vacuum chuck (804) previously described, can be used to support the end mill and to assist the plasma winding down the fluted portion.

Figure 16B shows an alternate embodiment 1620 of a technique for fabricating a coating on a round tool. In this case, an exemplary end mill 1622 (similar to the end mill 1602) is disposed on its side, with the nozzle and lasers coming from above (not shown). A plasma 1630 is formed at the tip of the

WO 95/20253

PCT/US95/00782

end mill, and is walked along the length of the fluted portion in a manner similar to what has been described above (with respect to causing relative motion of a selected area on a larger substrate). In this embodiment, the end mill should be rotated in concert with walking the plasma along the fluted portion, to ensure uniform coverage (coating fabrication) along the length of the fluted portion.

Figures 16C and 16D are side and end views, respectively, of an end mill 1642 (similar to 1602 or 1622) being further treated subsequent to depositing a thin film along the length of the fluted portion (in the manner of Figures 16A or 16B). In this case, it is desired to form a thick film coating in the flutes, adjacent the cutting edges so that the thick film aids in cutting, and the thin film aids in chip removal and reduction of cutting forces. Lasers and one or more secondary sources, both represented by the arrow 1644, are directed at a selected area (small spot) 1646 immediately adjacent the cutting edge. As the thick coating is being formed, the "spot" (selected area being treated) is advanced along the spiral (helical) cutting edge by moving the spot (e.g., from left-to-right, as viewed) in concert with rotating the end mill. As shown in Figure 16D, this results in an end mill having a "blanket" thin film diamond (or DLC) coating, and a thick film "gusset" of diamond (or DLC) along its cutting edge.

Figure 16E shows an alternate embodiment 1660 of a technique for fabricating a coating on a round tool. In this case, an exemplary end mill 1662 (similar to the end mill 1602) is disposed on its end, with the nozzle and lasers coming from above (not shown). In this case, a plasma 1664 is formed all along the fluted portion of the tool 1662 to effect coating fabrication without the need to walk along the length of tool.

WO 95/20253

PCT/US95/00782

Figure 16F shows an alternate embodiment 1680 of a technique for fabricating a coating on a round tool. In this case, an exemplary end mill 1682 (similar to the end mill 1602) is disposed on its side, with the nozzle and lasers coming from above (not shown). In this case, a plasma 1864 is formed all along the fluted portion of the tool 1662 to effect coating fabrication without the need to walk along the length of tool. Preferably, the tool is rotated while it is being coated to ensure uniformity in the coating process.

ADVANTAGES

The techniques of the present invention are advantageous for fabricating a number of coatings for any number of purposes, for example corrosion-resistant and erosion-resistant coatings, and coatings that are inert with respect to a hostile operating environment (e.g., steam boilers and the like). An advantage of the present invention is that entire surfaces of a substrate can be treated without heating the entire substrate. Prior art techniques which involve such "gross" heating of the substrate can cause, for example, an underlying steel substrate to lose its temper (hardness) when a diamond coating is applied (e.g., by a CVD process, or the like). Using the techniques of the present invention, refractory coatings can be fabricated on large surface areas, because the technique of the present invention can be performed in a continuous manner, in an ambient environment. Generally, the advantages of the present invention include:

(a) A higher deposition rate is achieved, such as on the order of one or more millimeters per hour.

(b) Greater adhesion (e.g., 50kg/mm²) is provided for cutting tools.

(c) Crystalline coatings can be fabricated, such as with a crystal lattice structure, and with an SP²- or SP³-bonded carbon structure, and with a controlled mix, if desired.

WO 95/20253

PCT/US95/00782

(d) There is no pre-heating or cool-down time required.

(e) The process does not require a vacuum environment. Hence, there is no theoretical limit on the size of the substrate. Further, mechanisms for manipulating the substrate
5 are more readily accommodated in an ambient (versus vacuum) environment.

(f) The parts can be manipulated, various layer thicknesses can be achieved, and the coating can be applied to specific areas of the part without masking.

10 (g) The coating (e.g., diamond) will adhere well to substrates having more than 10% cobalt content, thereby substantially eliminating the need for specialty substrates.

(h) Stainless steel can easily be coated using the techniques of the present invention.

15 (i) Steel can easily be coated using the techniques of the present invention, thereby eliminating requirements (in the first instance) for stainless.

(j) The inventive technique works well for coating the inside diameters (ID, bore) of tubes, including those having a
20 relatively high length:diameter (L-to-D) ratio.

(k) Sculpting and texturing may be accomplished during the coating process, thereby eliminating post-finishing steps of the prior art.

25 (l) The technique of the present invention can also be heteroepitaxial.

(m) The technique of the present invention effectively coats all sides evenly, or selectively, for any shape substrate.

(n) There is no Raman variance evident when employing the technique of the present invention, with substrates having
30 various compositions, to obtain a desired composite materials.

For example, Raman spectral analysis reveals that substrates of various compositions have little or no effect on diamond coatings produced by techniques of the present invention.

35 (o) Substrates having complex geometries can be treated, and various dopants (e.g., boron) can be introduced into the

WO 95/20253

PCT/US95/00782

surface treatment.

(p) Substrates can be pre-treated to characterize their surfaces for further application of a coating, by any suitable technique.

5 The present invention is applicable to treating any of a number of substrates, including metal and non-metal substrates (non-metal substrates include ceramics and polymeric substrates). Specific materials that can be treated, or introduced into the reaction system, include, but are not limited to:

- 10 • metals (B, Al, Ti, Nb, Ta, Cr, Mo, W, Re, Hf, etc.);
- graphite and carbides (C, B₄C, SiC, TiC, Cr₃C₂, WC, hafnium carbide, etc.);
- nitrides (BN, TiN, TaN, Si₃N₄, etc.);
- 15 • boron and borides (B, TaB₂, TiB₂, WB, FeB, NiB, etc.);
- Silicon and silicides (Si, and the different silicides of Mo, Fe, Ni, etc.);
- oxides (Al₂O₃, SiO, SiO₂); and
- 20 • organic compounds (PTFE, Kevlar, Polyimides, Liquid Crystalline Polymers, Polyethyltetrathalate).

 As mentioned hereinabove, an advantage of the techniques of the present invention is that there is no post-process finishing required to obtain a desired surface texture. The ultraviolet laser itself (for example) can be used to ablate the surface to obtain virtually any texture ranging from rough to optically-smooth, simply by controlling its output and duration. Furthermore, by using the techniques of the present invention, there is no need to seed the substrate (for subsequent growth of a coating), and there is an unprecedented ability to control crystal orientation. Moreover, both pre-treatment and post-finishing can be performed in-situ (as part of the overall process).

WO 95/20253

PCT/US95/00782

In the prior art deposition techniques, post-finishing steps would be required to obtain a texture smoother than the texture achieved by deposition. For example, an abrasive would be used to polish the coated surface of the substrate. The use
5 of an abrasive, however fine, will leave traces (evidence) of the substrate having been polished in the form of scratches. A subsequent ultraviolet laser, ion beam, smoothing or polishing process can also be required.

By circumventing the use of abrasives, and the like, in
10 post-process finishing steps, the resulting substrate (product-by-process) will not exhibit such scratches and will have a non-directional surface finish.

Although the invention has been illustrated and described in detail in the drawings and foregoing description, the same
15 is to be considered as illustrative and not restrictive in character - it being understood that only preferred embodiments have been shown and described, and that all changes and modifications that come within the spirit of the invention are desired to be protected.

WO 95/20253

PCT/US95/00782

CLAIMS

What is claimed is:

1. Method of surface-treating a surface of a substrate, comprising:

5 directing at least one beam from corresponding at least one laser at a surface of a substrate to mobilize a constituent element of the substrate from a subsurface region of the substrate towards the surface of the substrate.

2. Method, according to claim 1, further comprising:

10 providing sufficient energy in the at least one beam to vaporize the constituent element.

3. Method, according to claim 1, further comprising:

15 continuing to direct the at least one beam at the surface of the substrate to react the vaporized constituent element.

4. Method, according to claim 1, further comprising:

20 continuing to direct the at least one beam at the surface of the substrate to diffuse the reacted vaporized constituent element back into the subsurface region of the substrate.

5. Method, according to claim 4, further comprising:

25 in conjunction with reacting the vaporized constituent element, directing a secondary element at the surface of the substrate to form a composite material with the vaporized constituent element.

6. Method, according to claim 5, further comprising:

continuing to direct the at least one beam at the surface of the substrate to fabricate a coating on the surface

WO 95/20253

PCT/US95/00782

of the substrate.

7. Method, according to claim 1, wherein:
the substrate is a flat cutting insert.

8. Method, according to claim 1, wherein:
the substrate is cemented tungsten carbide.

9. Method, according to claim 1, wherein:
the substrate is a round cutting tool.

10. Method, according to claim 1, wherein:
the at least one beam is three beams provided by an
excimer laser, an Nd:YAG laser and a CO₂ laser, acting in
concert with one another.

11. Method, according to claim 10, wherein:
the excimer laser is operated at a power output up to
200 W, with a pulse energy up to 500 mJ, at a pulse sequence
frequency up to 300 Hz, with an energy density of up to 30
mJ/mm², and a pulse length (duration) up to 26 ns;

the Nd:YAG laser is operated at a power output up to
1500 W, with a pulse energy up to 150 J; and

the CO₂ laser is operated at a power output on the
order of 500 - 10,000 W, with an energy density up to 0.32
J/cm².

12. Method, according to claim 11, wherein:
the pulses from the excimer and Nd:YAG lasers are
coordinated with one another.

13. Method, according to claim 10, wherein:
the beam from the excimer laser has a rectangular
profile;

WO 95/20253

PCT/US95/00782

the beam from the Nd:YAG laser has a circular profile; and

the beam from the CO₂ laser has a circular profile.

14. Method, according to claim 13, further comprising:

5 causing the circular beams to cover a relatively large portion of the surface of the substrate;

causing the rectangular beam to cover a relatively small portion of the surface of the substrate, said relatively small portion being located within the relatively large portion.

10 15. Method, according to claim 14, further comprising:

moving the substrate relative to the beams to cause the relatively small portion to be scanned across the surface of the substrate.

16. Method of pre-treating a substrate for subsequent

15 formation of a coating on a surface of the substrate, comprising:

directing an excimer laser at the surface of the substrate; and

20 while directing the excimer laser at the surface of the substrate, flooding the substrate with an inert gas.

17. Method, according to claim 16, wherein:

the substrate has tungsten carbide grains surrounded by cobalt.

18. Method, according to claim 17, further comprising:

25 directing the excimer laser at the surface of the substrate for a sufficient time to expose the tungsten carbide grains.

WO 95/20253

PCT/US95/00782

19. Method, according to claim 17, wherein:

the inert gas is nitrogen; and

further comprising:

5 while directing the excimer laser at the surface of
the substrate, forming complexes of carbon, nitride and stable
complex cobalt nitride at the surface of the substrate.

20. Method, according to claim 16, further comprising:

10 while directing the excimer laser at the surface of
the substrate, causing a predetermined grain orientation at the
surface of the substrate.

WO 95/20253

PCT/US95/00782

Figure 1

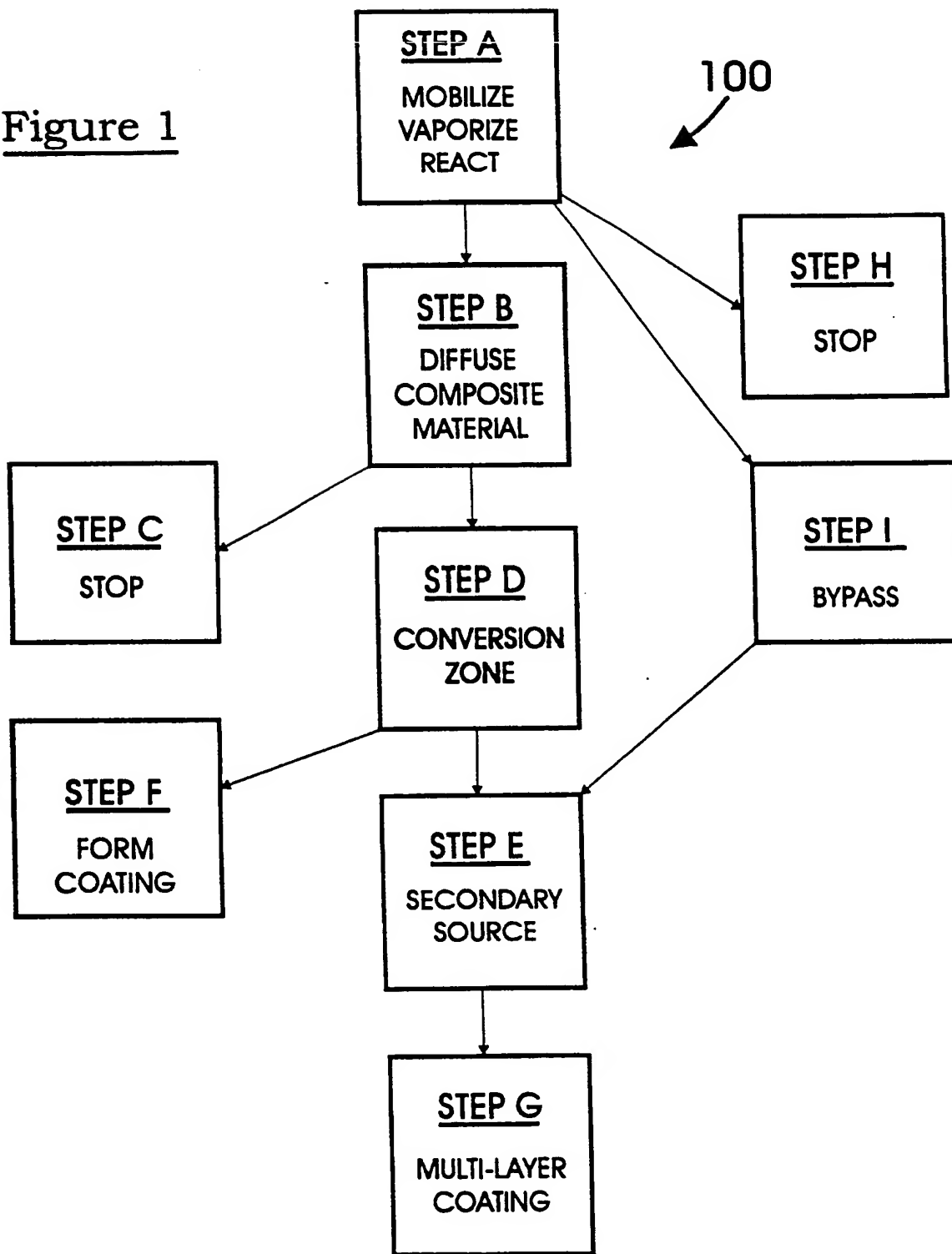


Figure 2A

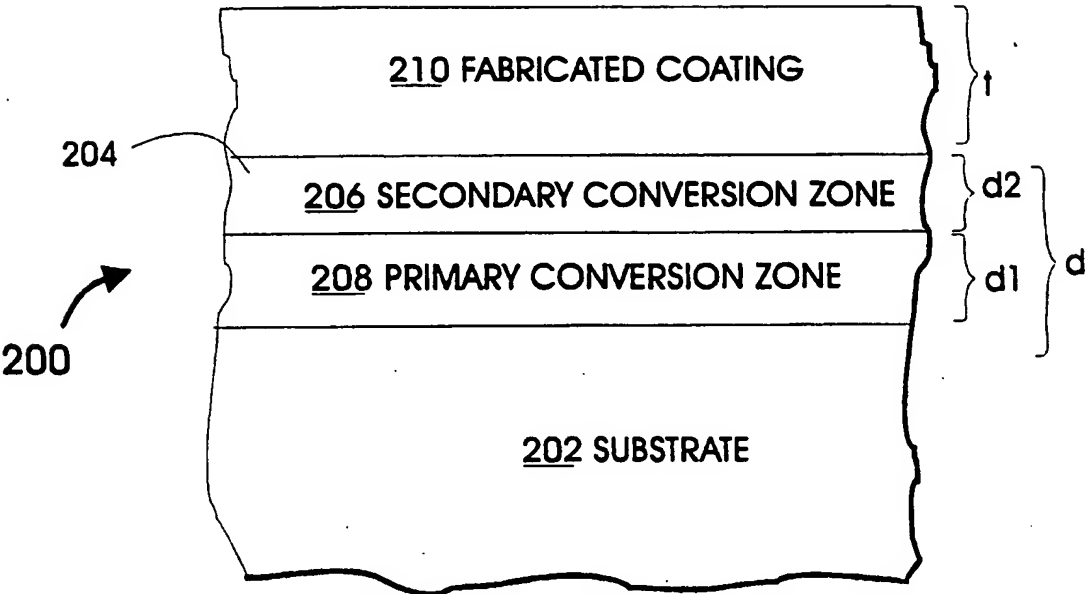


Figure 2B

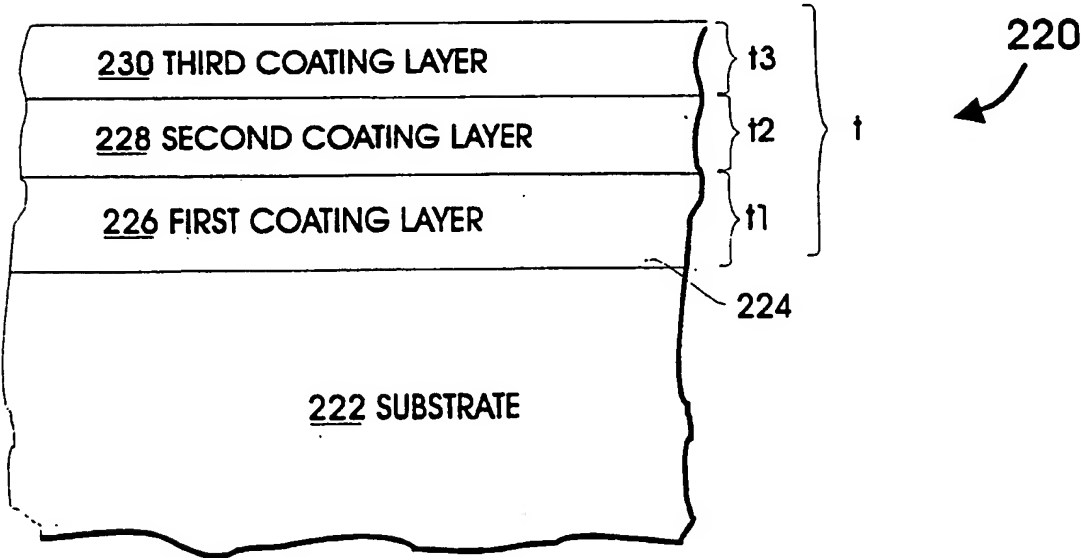


Figure 3

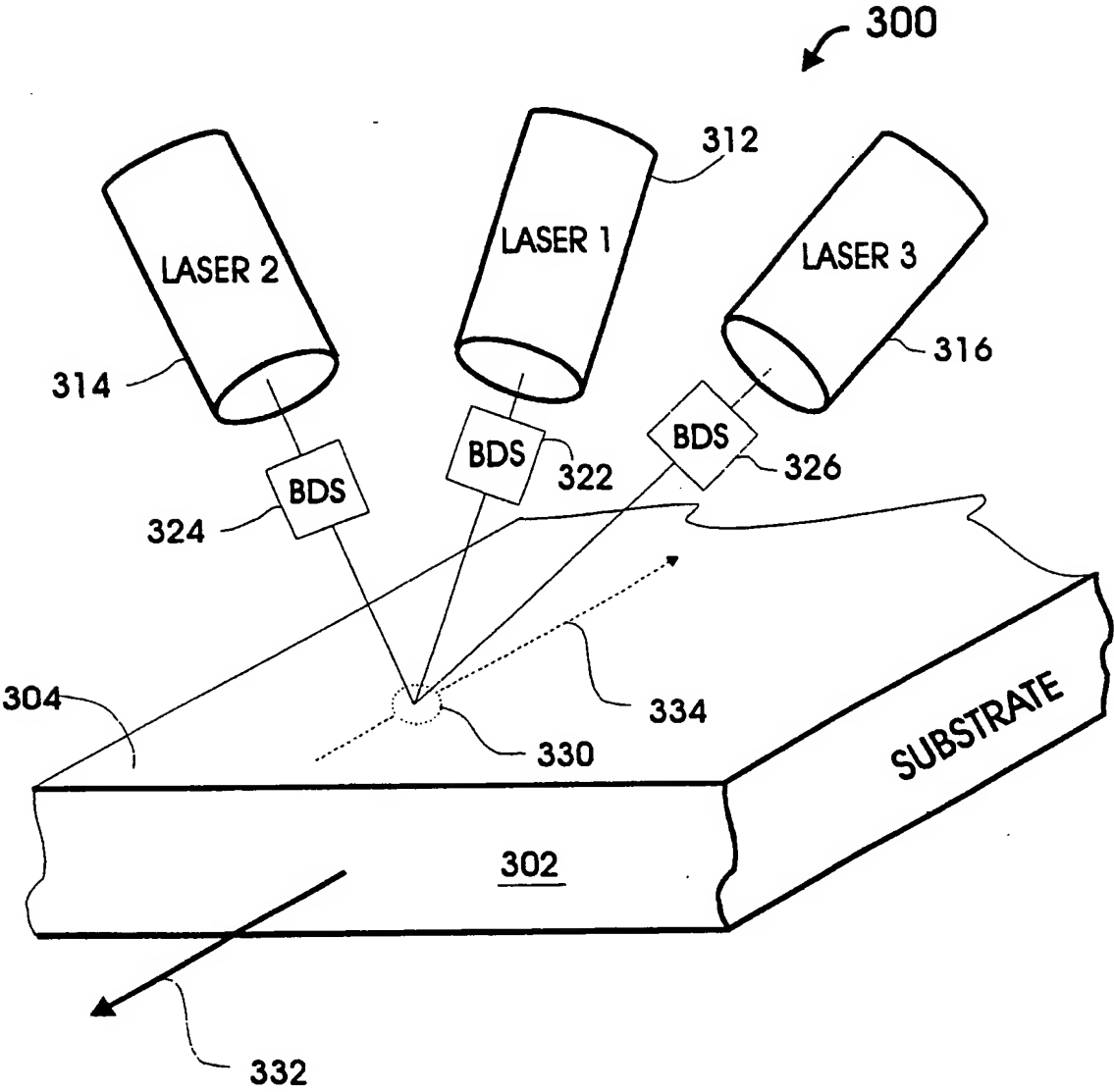


Figure 4

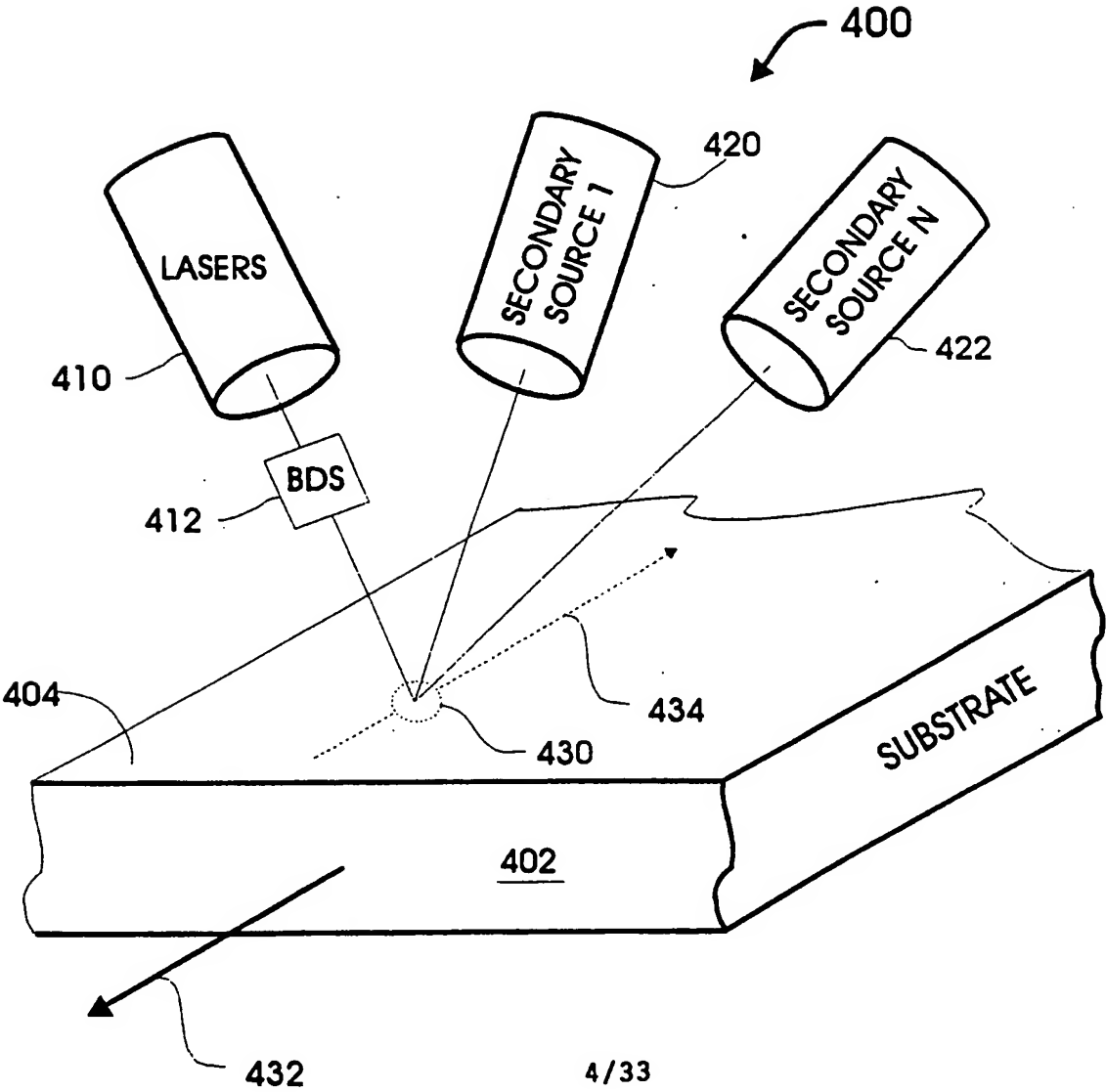
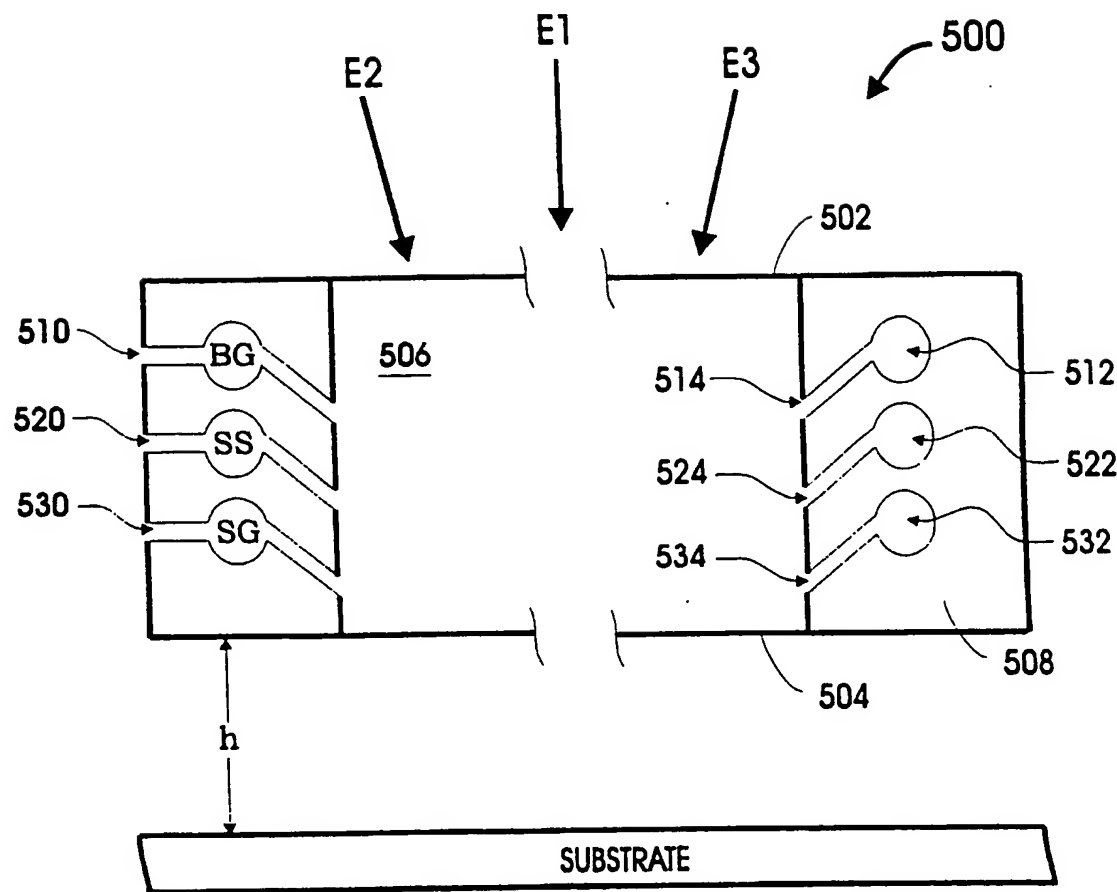


Figure 5



WO 95/20253

PCT/US95/00782

Figure 5A

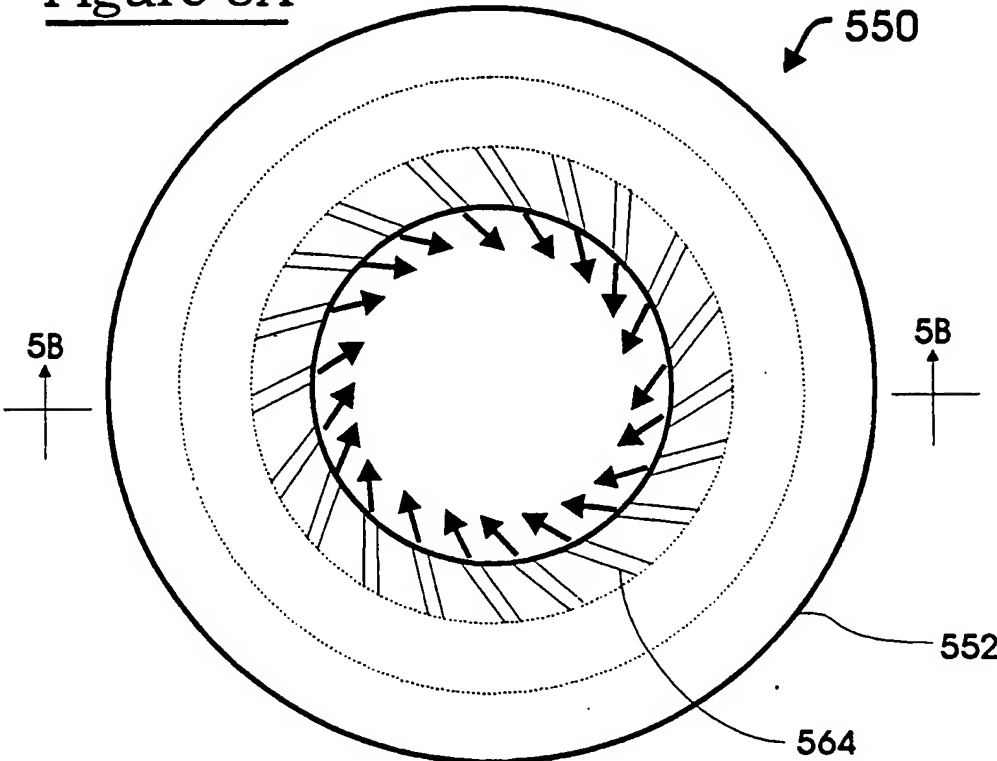


Figure 5B

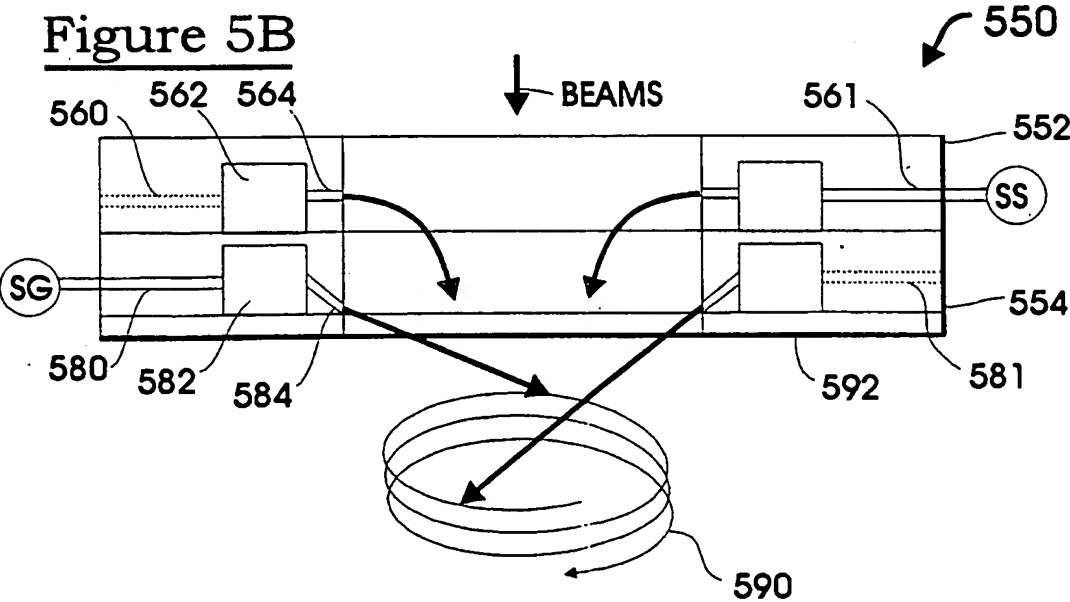


Figure 6A
(PRIOR ART)

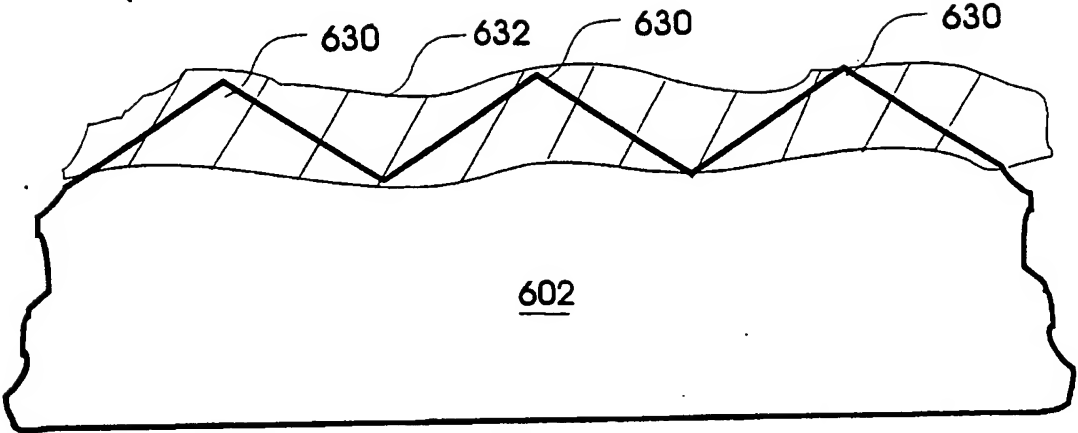
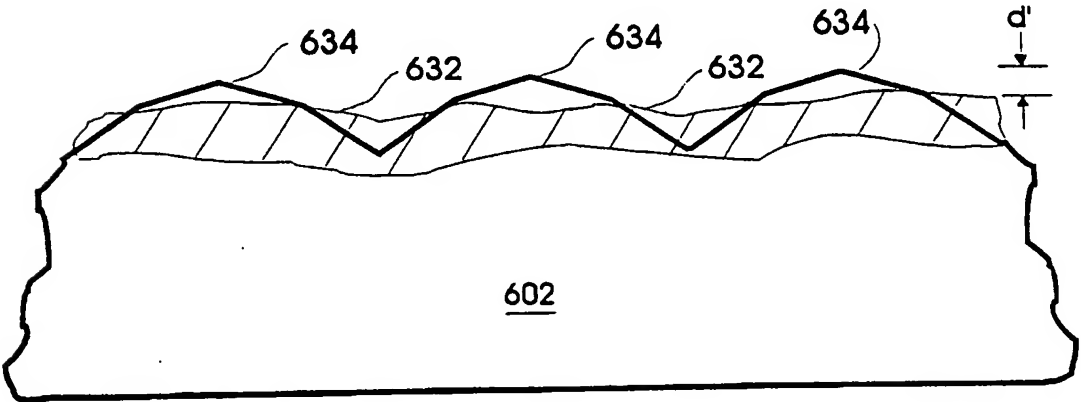


Figure 6B



WO 95/20253

PCT/US95/00782

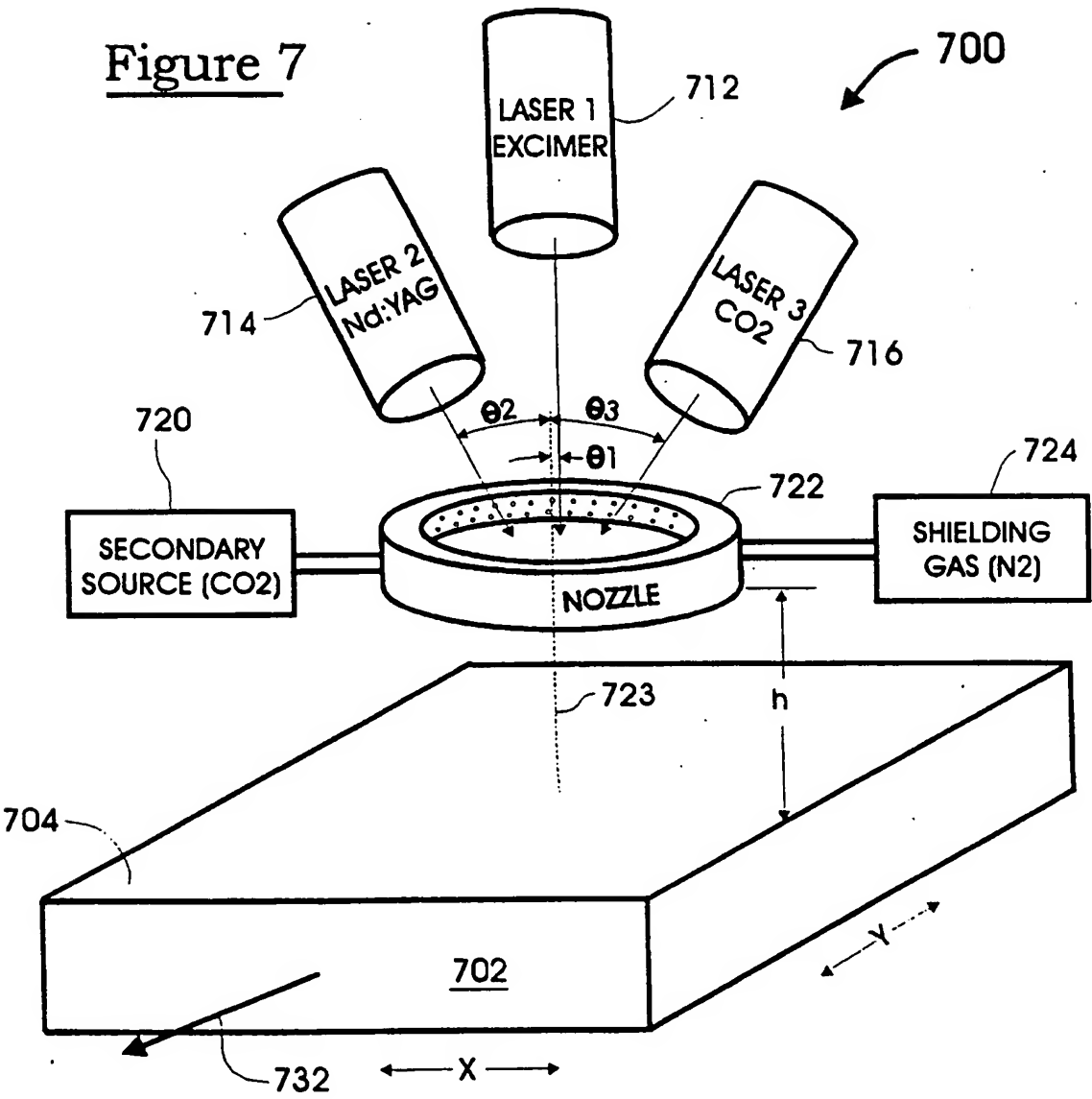


Figure 8

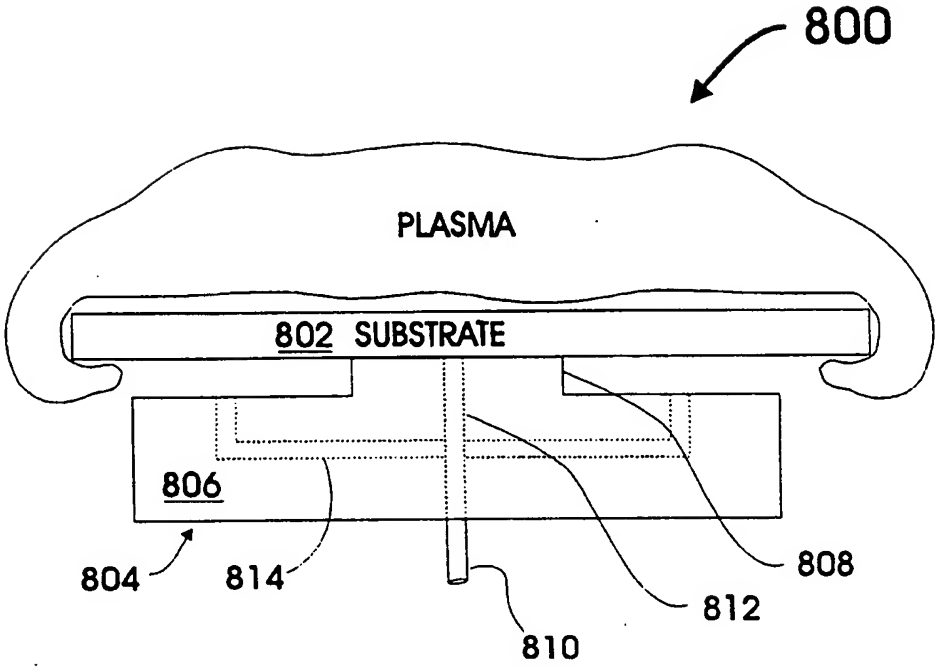


Figure 9

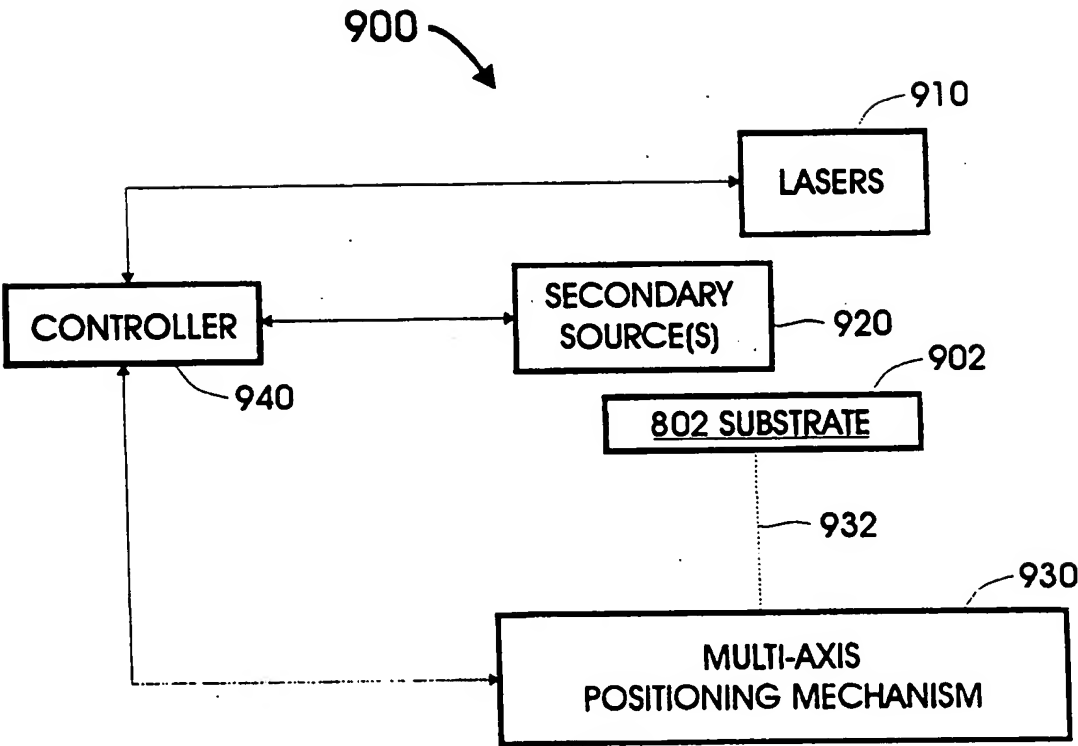
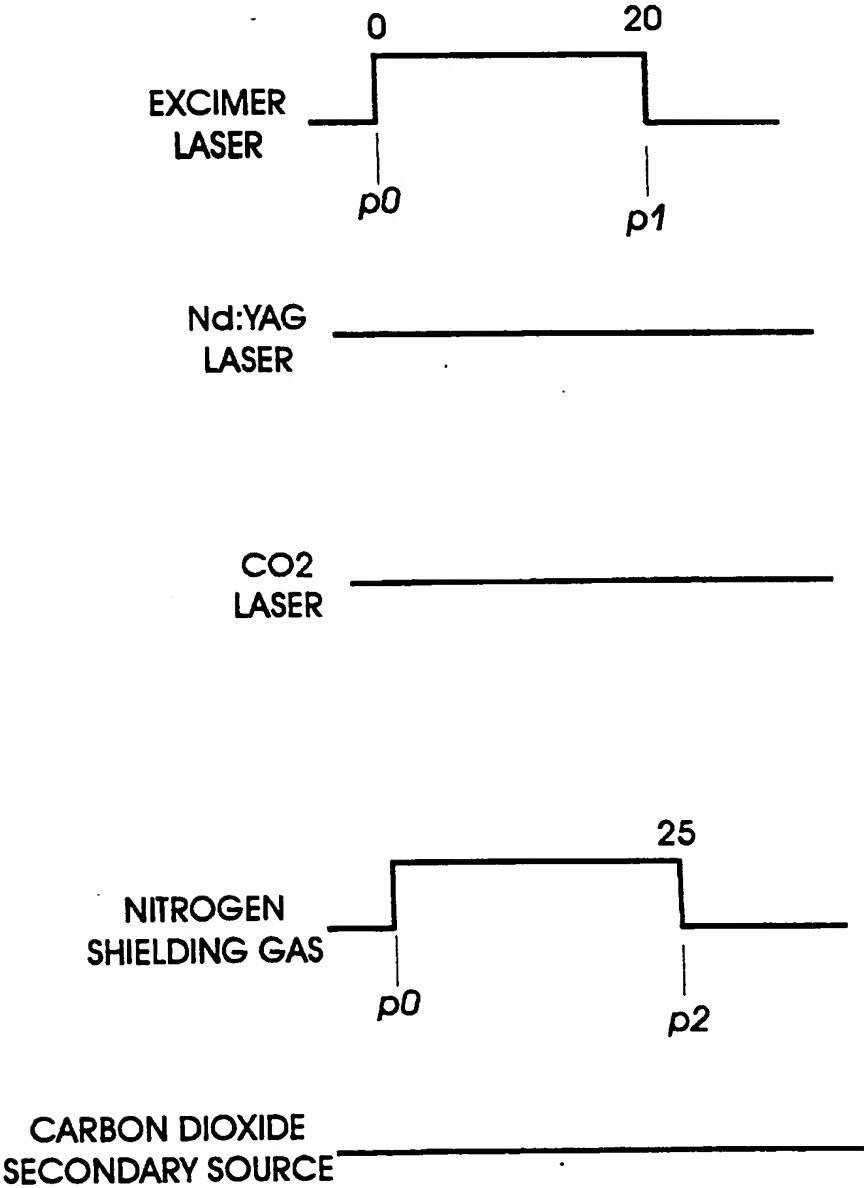


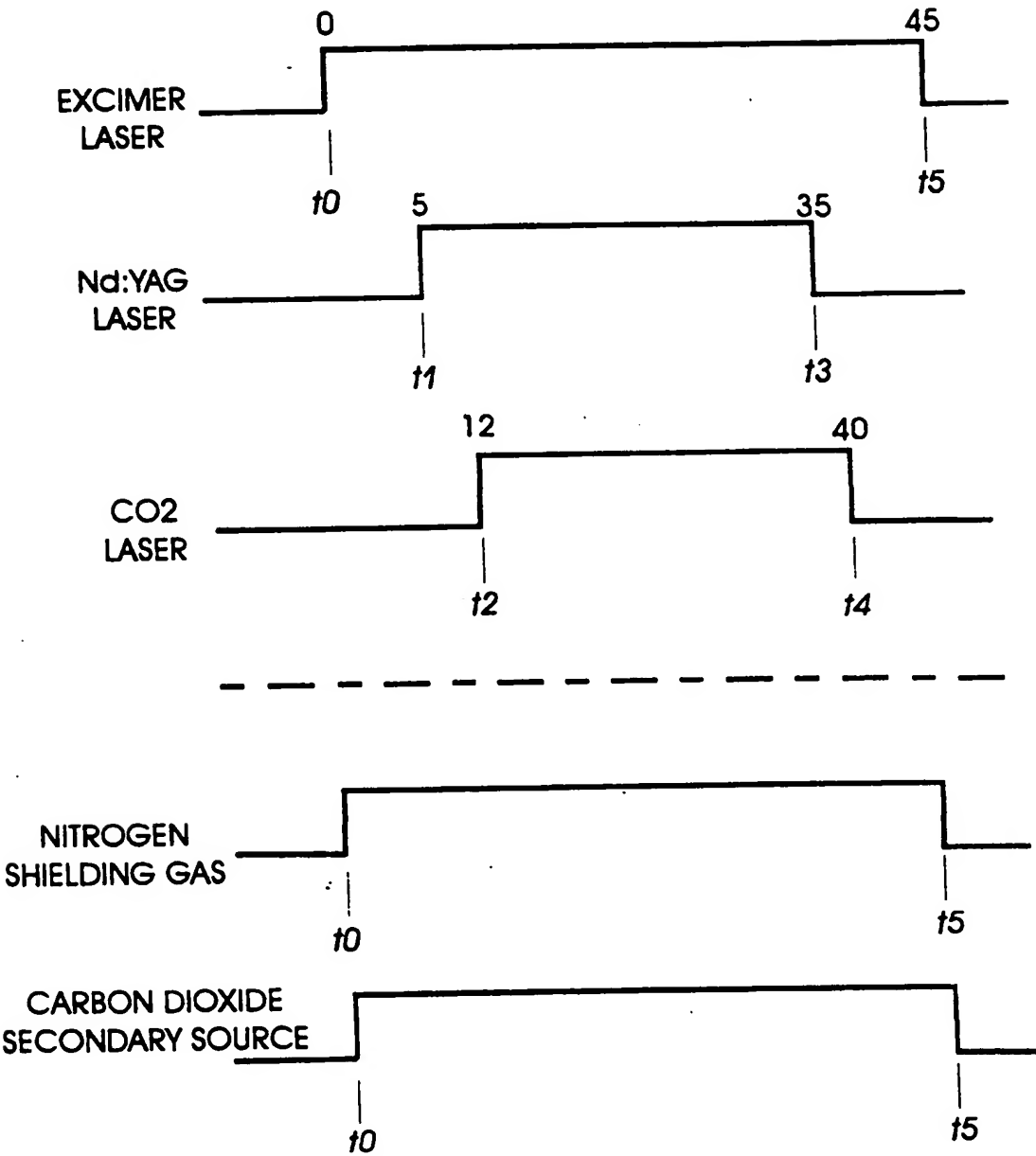
Figure 10
(PRE-TREATMENT ONLY)



WO 95/20253

PCT/US95/00782

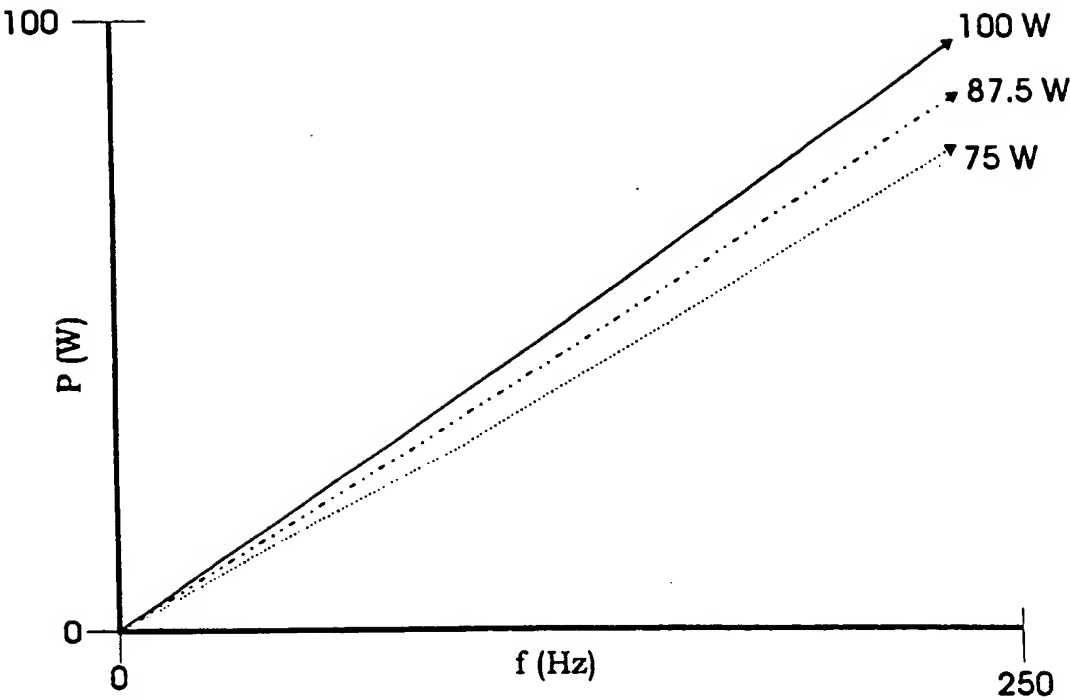
Figure 10A
(PRE-TREAT AND COAT)



WO 95/20253

PCT/US95/00782

Figure 10B
EXCIMER POWER OUTPUT



WO 95/20253

PCT/US95/00782

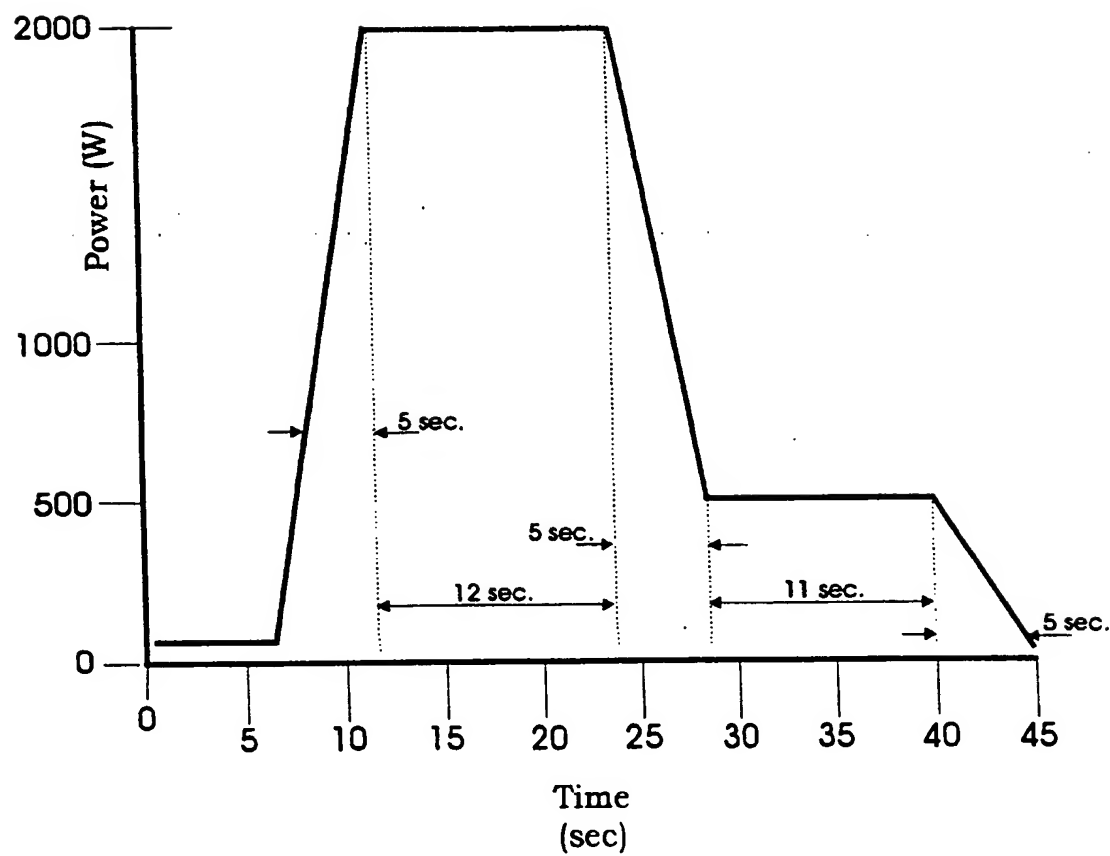
Figure 10C
Nd:YAG (PROGRAMS DATA)

PROGRAM NUMBER	FREQUENCY (Hz)	BURST TIME	PUMP PULSE ENERGY	MAXIMUM FREQUENCY (Hz)
1	15	40	14	46.5
2	32	0	21	32.0
3	1	0	25	27
4	120	15	5	120
5	55	30	12	55.5
6	20	30	21	32.4
7	120	15	5	130.4
8	25	450	14	46.5
9	5	50	89	7.7
10	60	100	9	69.7
11	7.5	50	89	7.7
12	1	22	69	9.9
13	10	16	16	41.6

WO 95/20253

PCT/US95/00782

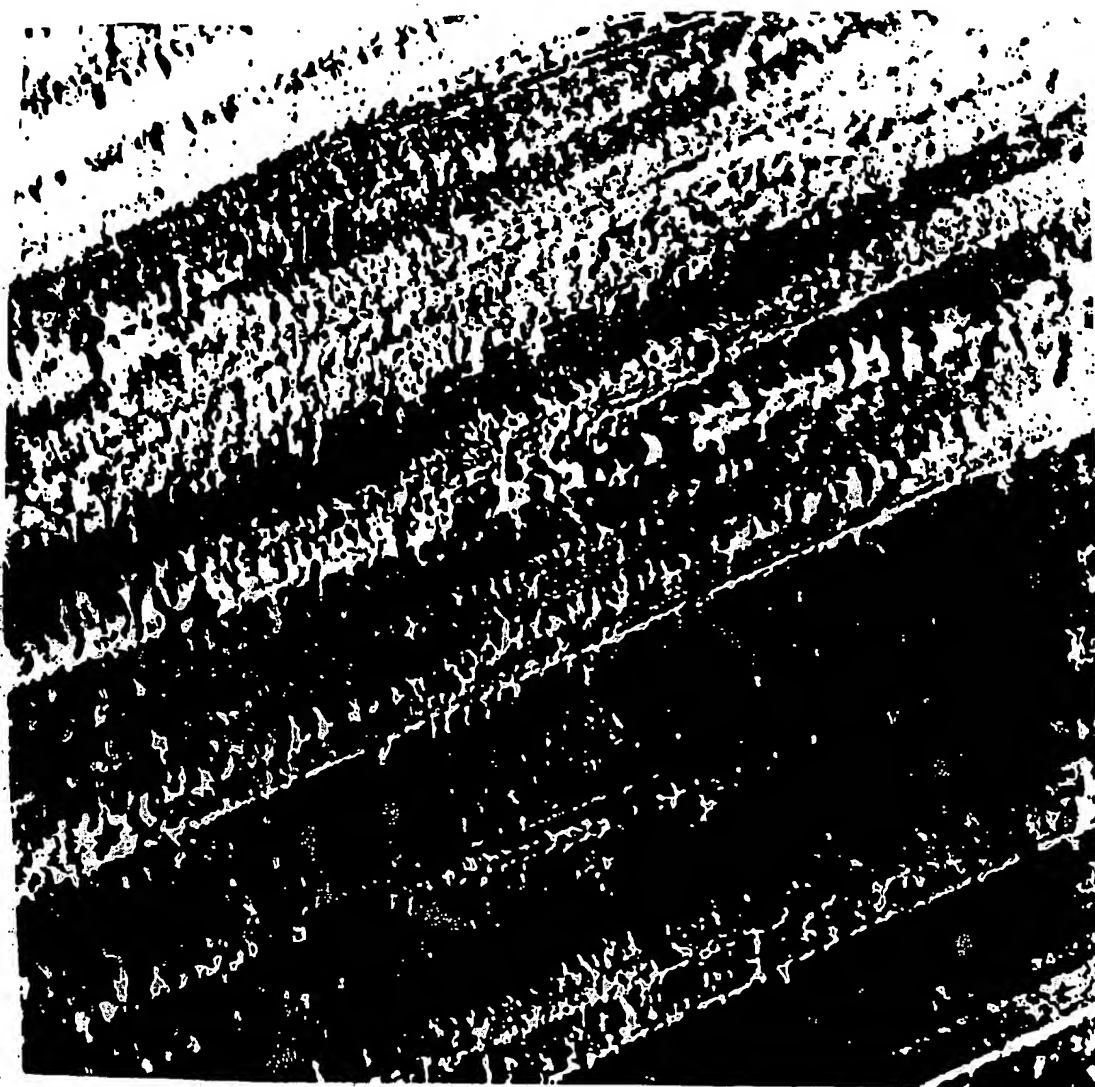
Figure 10D
CO2 LASER
POWER DIAGRAM



WO 95/20253

PCT/US95/00782

Figure 11A
(Prior Art)



WO 95/20253

PCT/US95/00782

Figure 11B



WO 95/20253

PCT/US95/00782

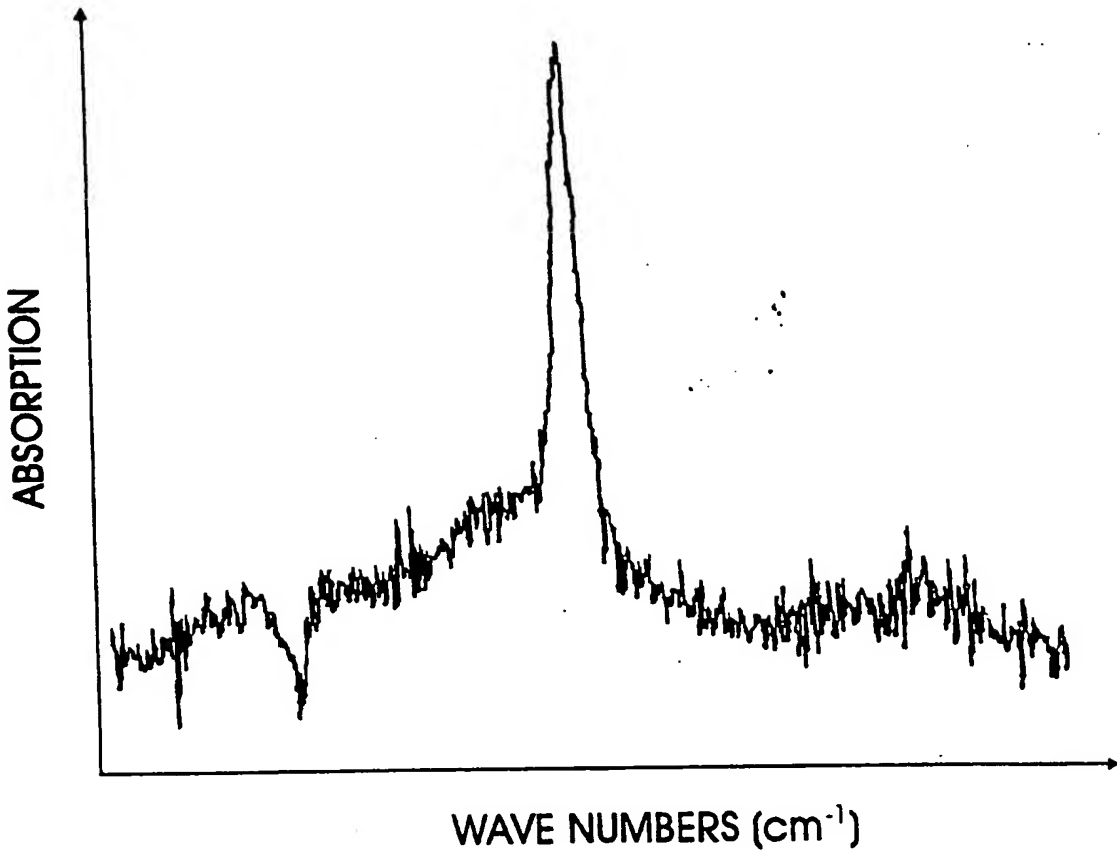
Figure 11C



WO 95/20253

PCT/US95/00782

Figure 11D



WO 95/20253

PCT/US95/00782

Figure 11E

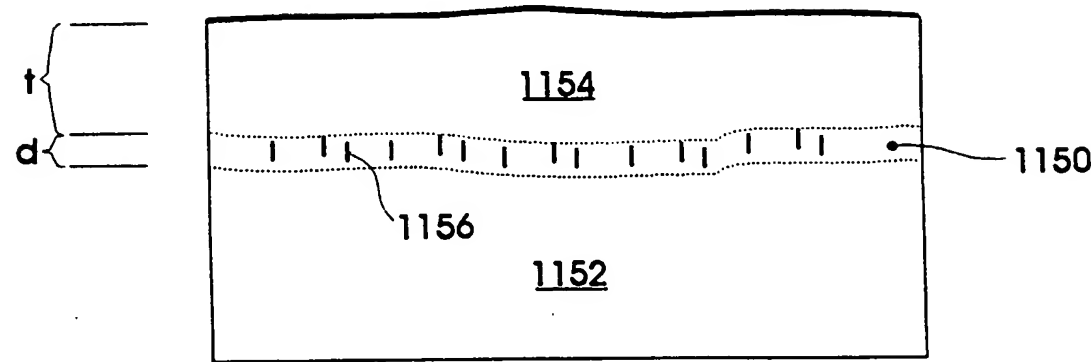


Figure 11F



Figure 12A

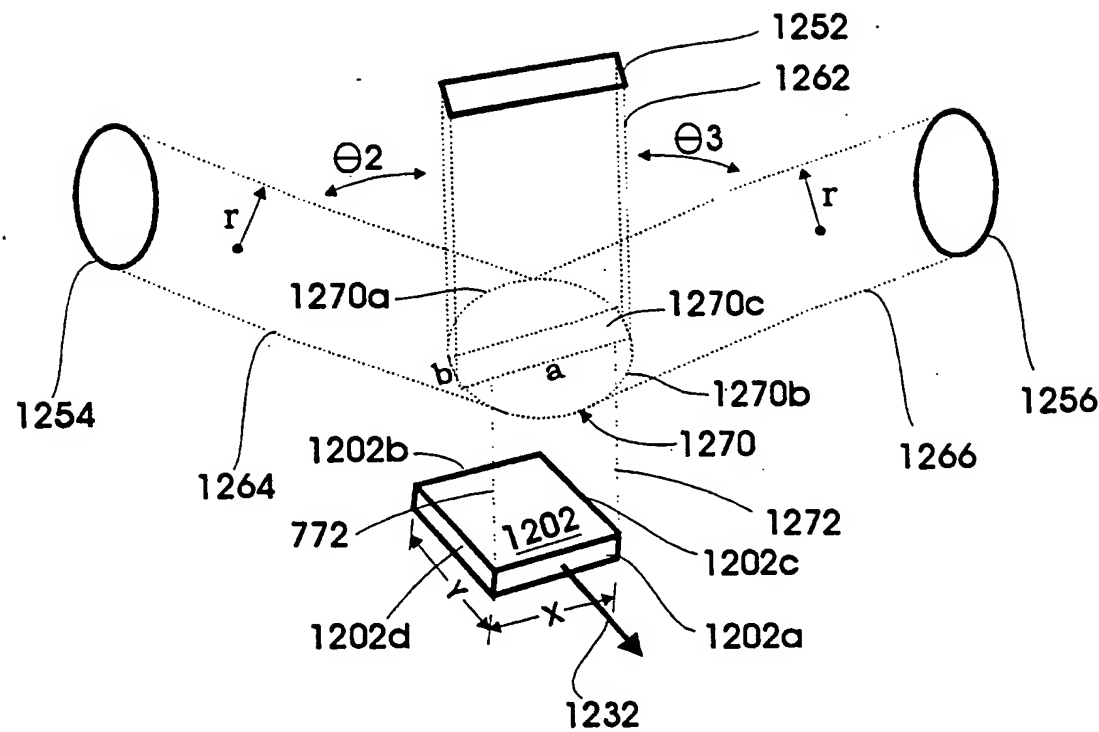


Figure 12B

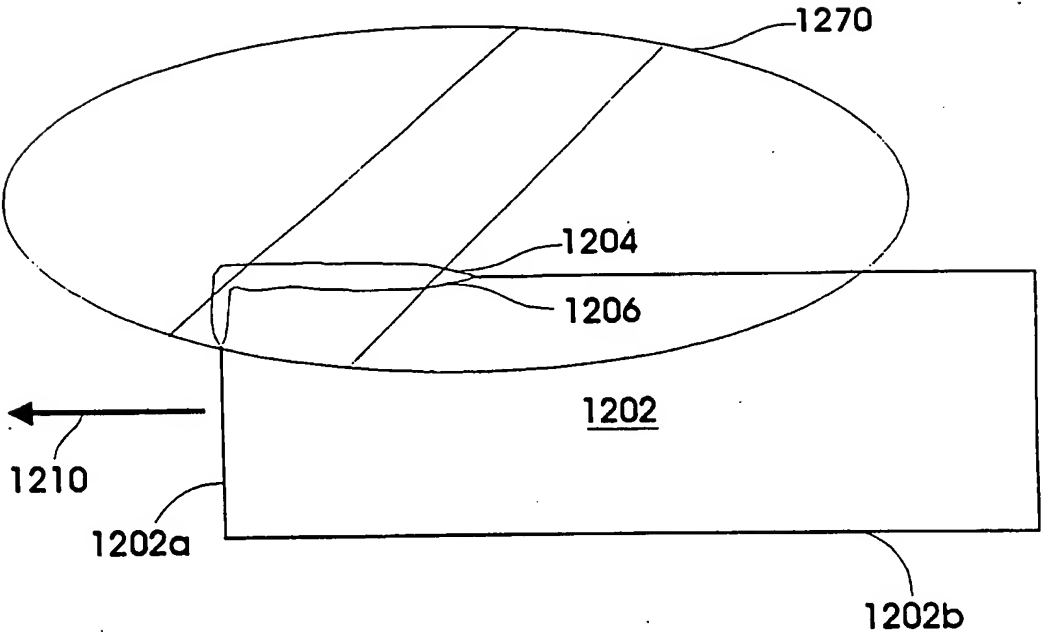


Figure 13A

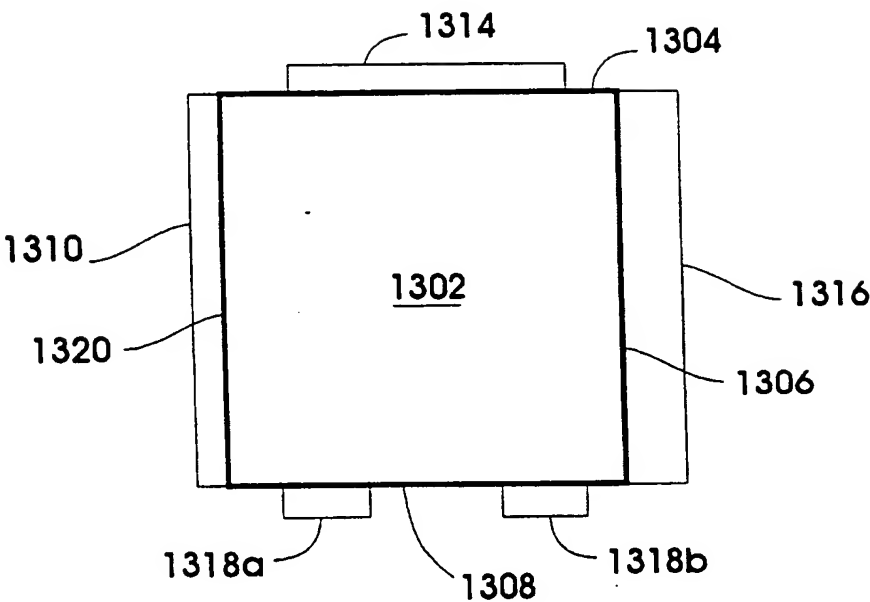


Figure 13B

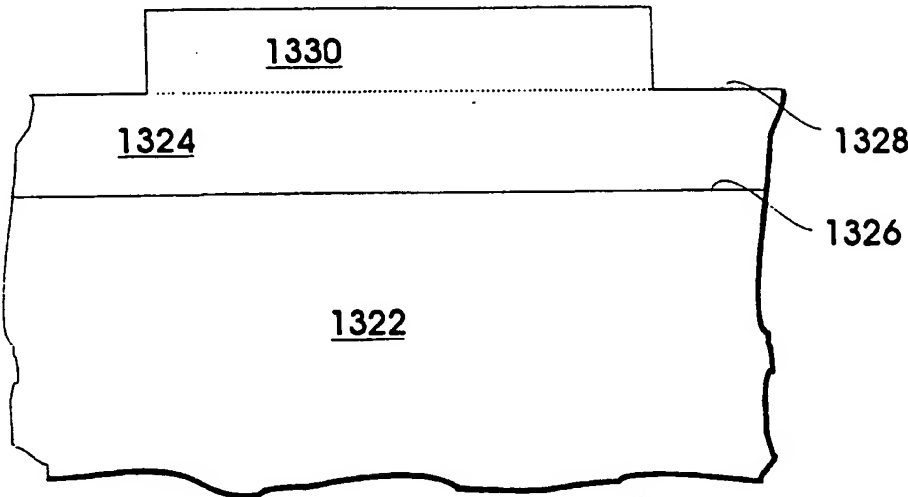


Figure 13C

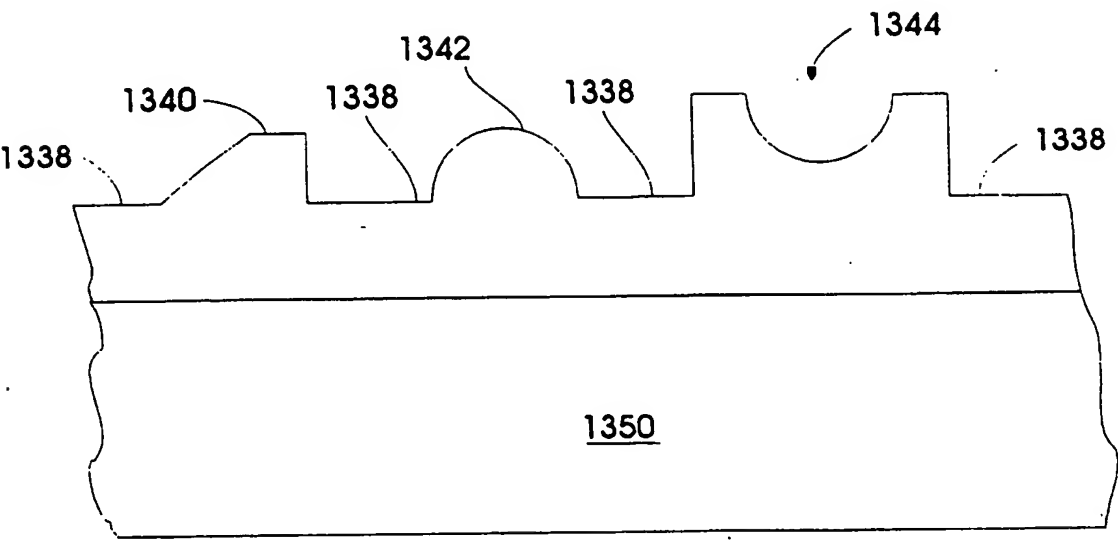


Figure 13D

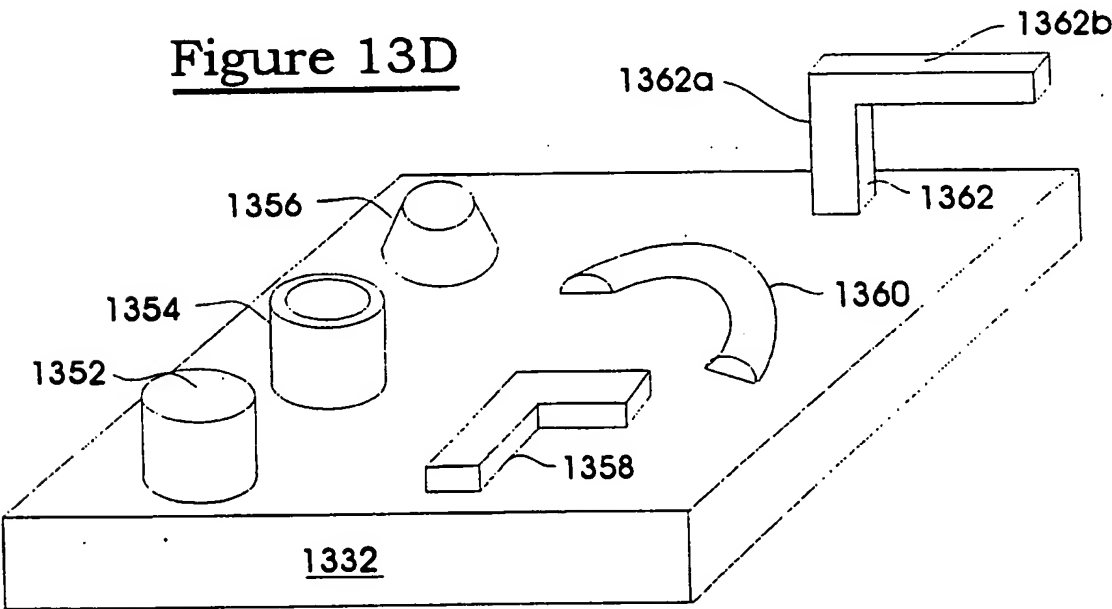


Figure 13E

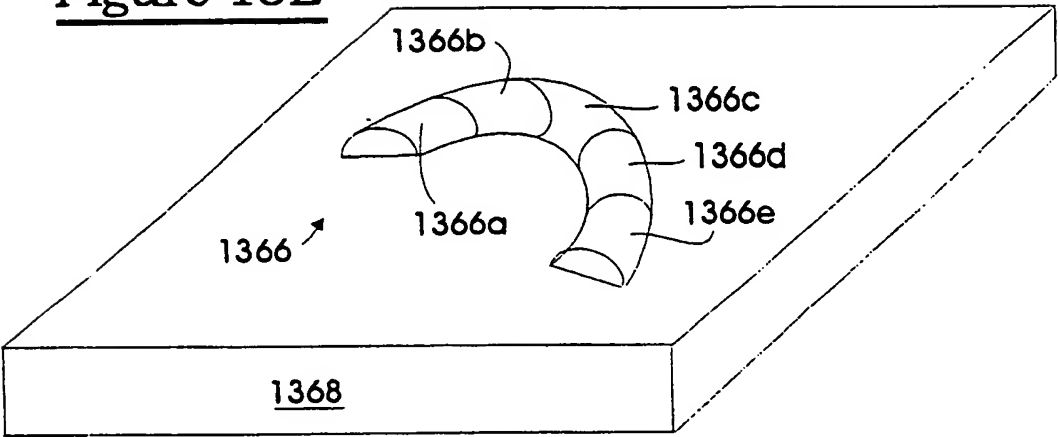
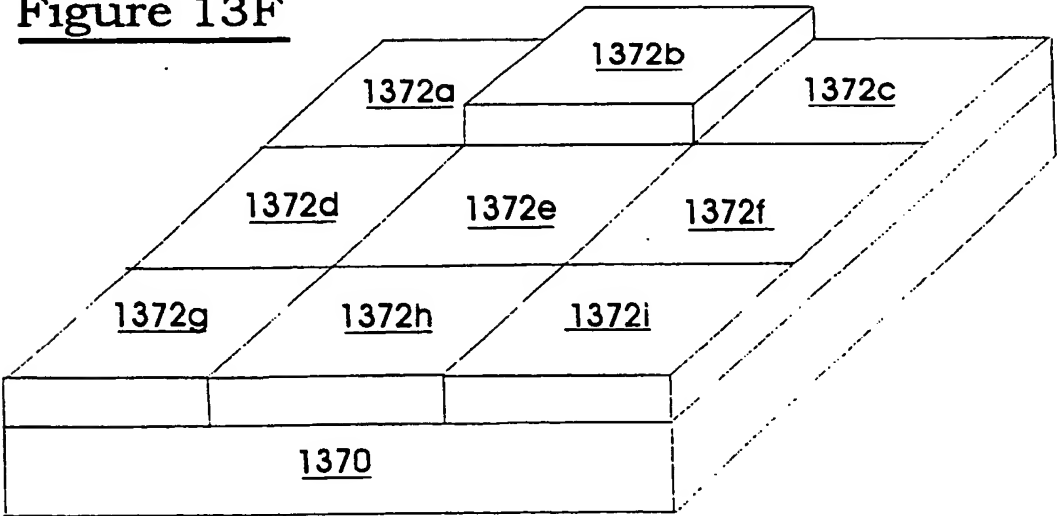


Figure 13F



WO 95/20253

PCT/US95/00782

Figure 13G

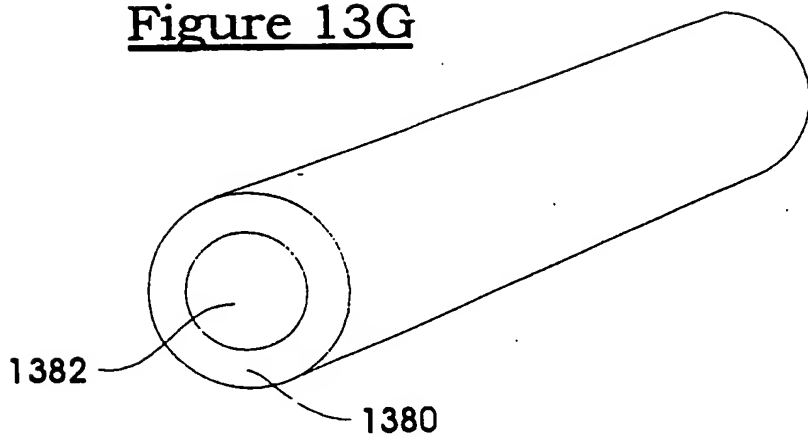
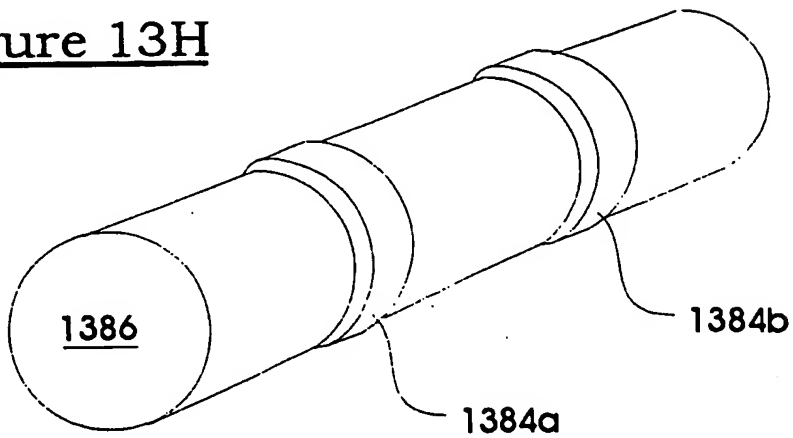


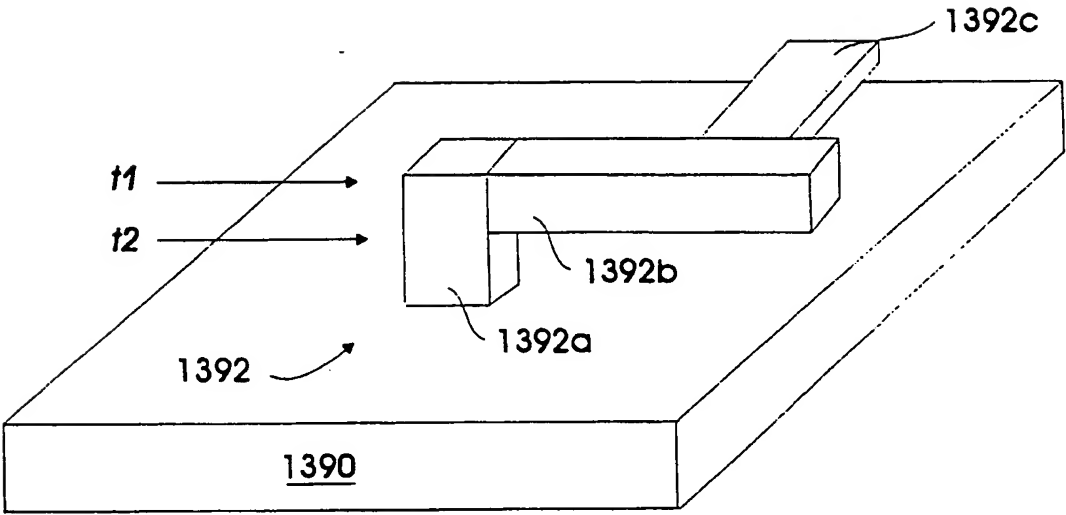
Figure 13H



WO 95/20253

PCT/US95/00782

Figure 13I



WO 95/20253

PCT/US95/00782

Figure 14A

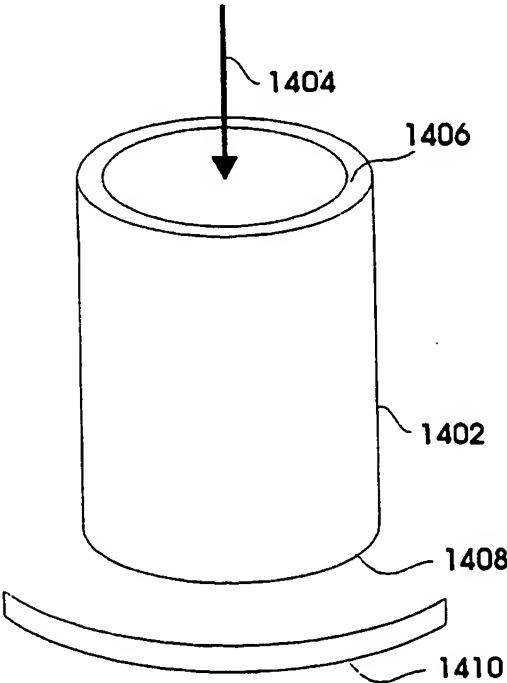


Figure 14B

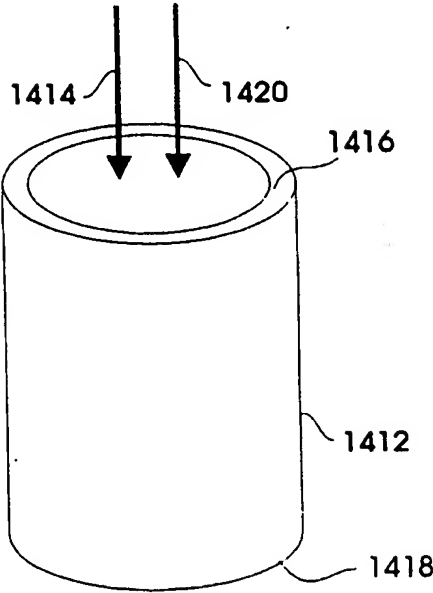


Figure 15A

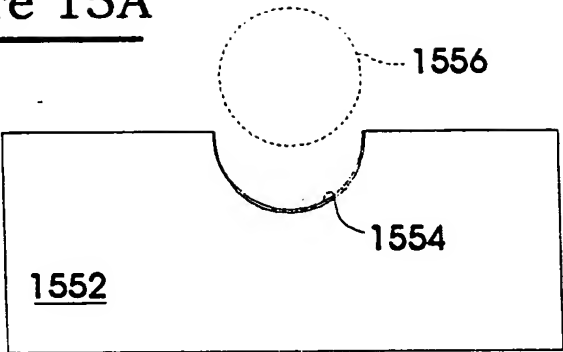
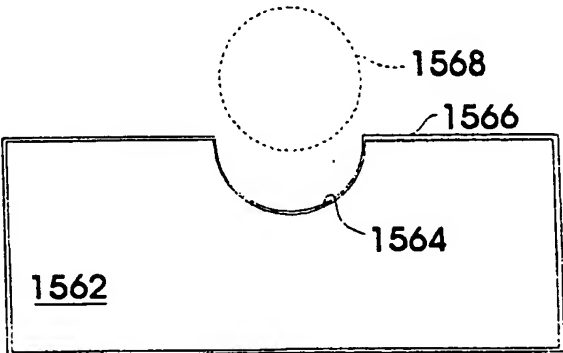


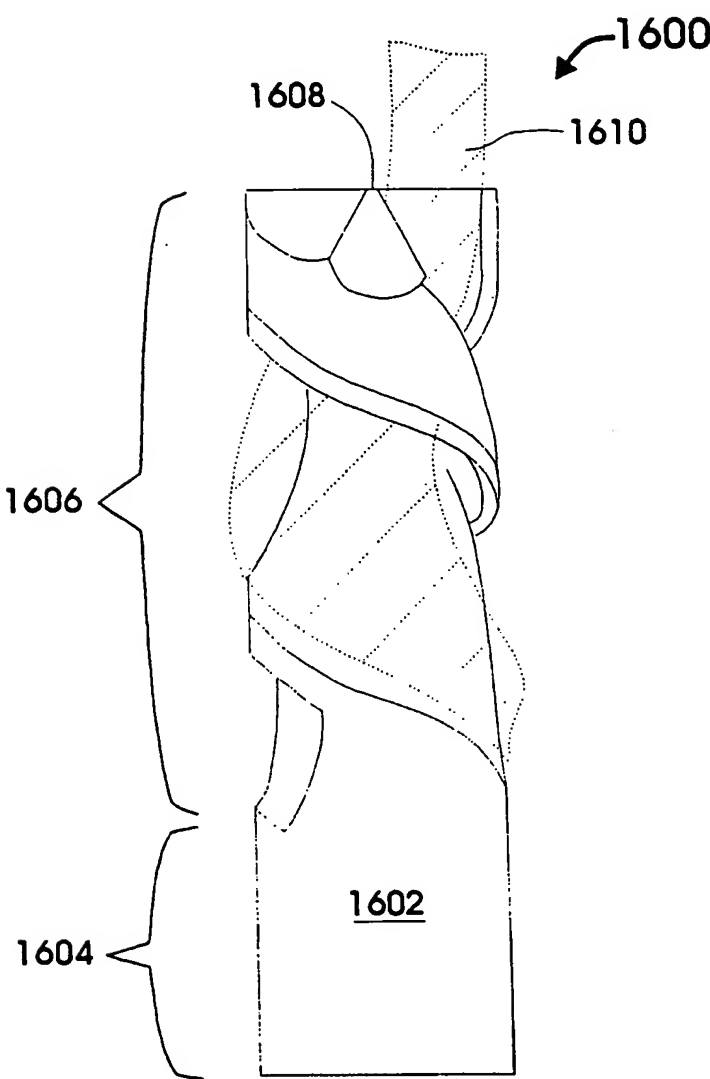
Figure 15B

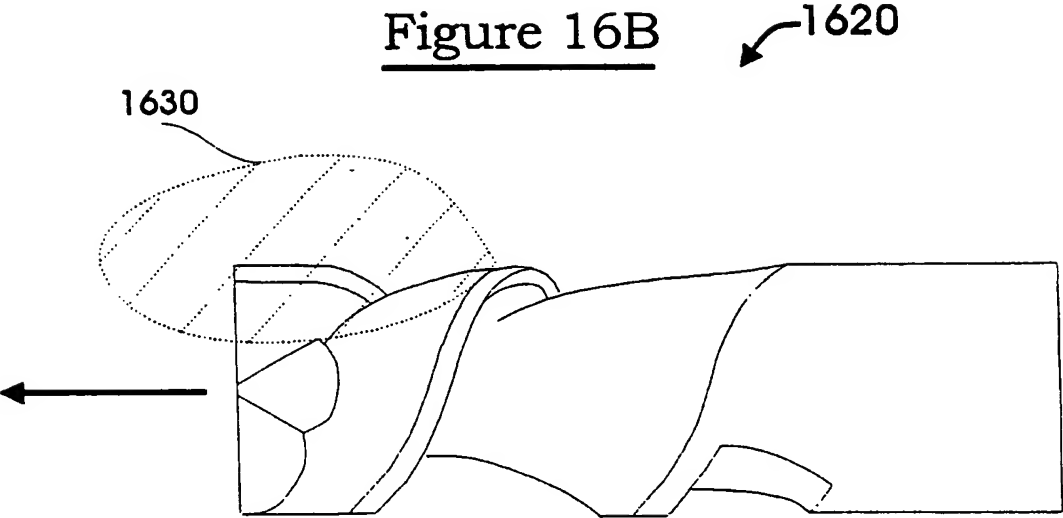


WO 95/20253

PCT/US95/00782

Figure 16A





WO 95/20253

PCT/US95/00782

Figure 16C

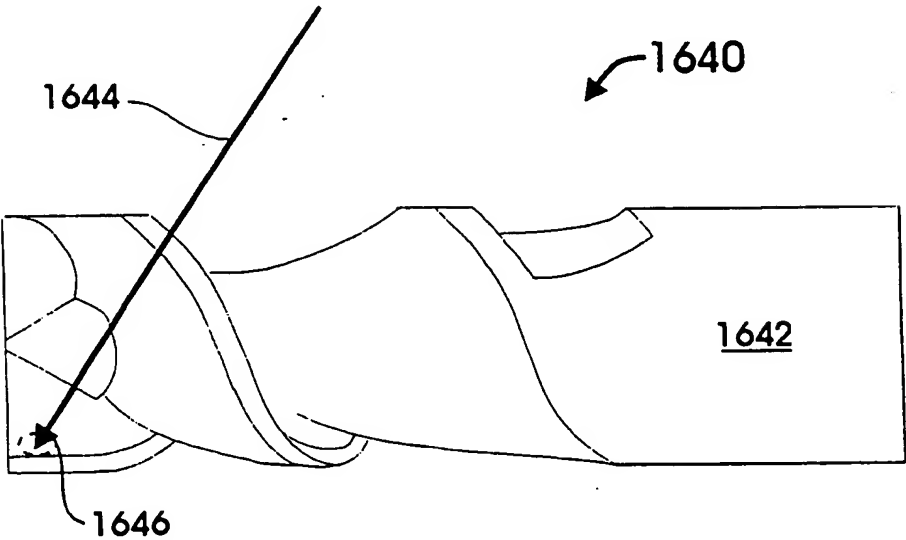
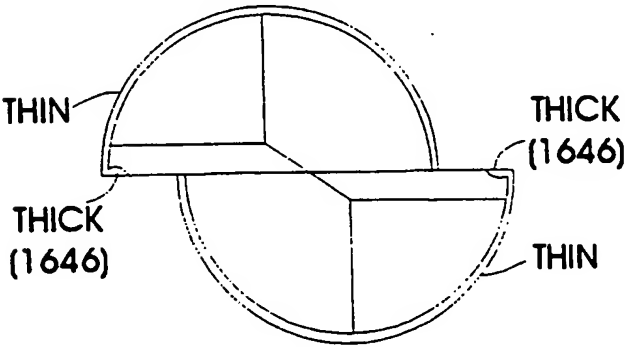


Figure 16D



WO 95/20253

PCT/US95/00782

Figure 16E

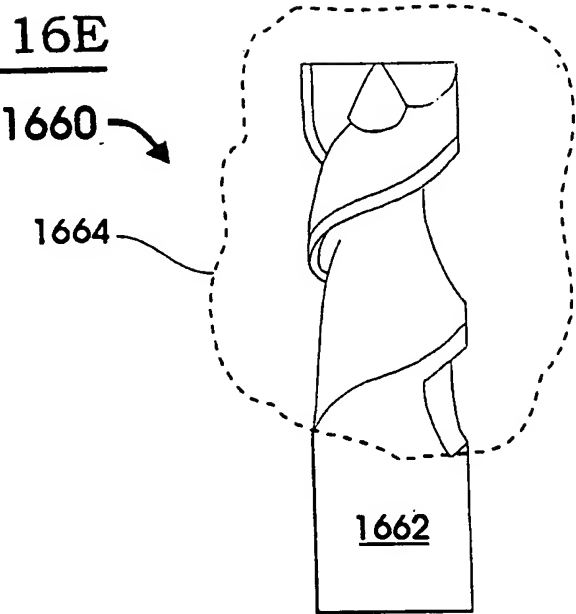
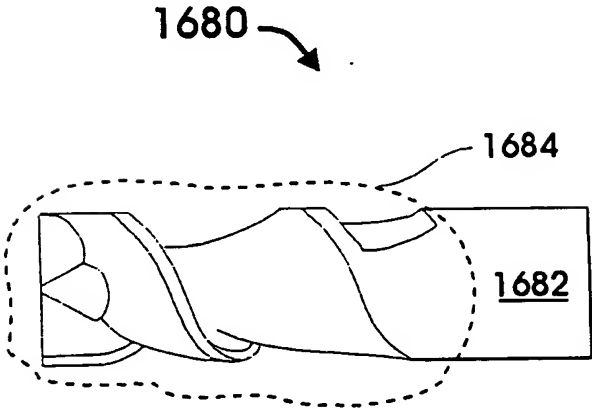


Figure 16F



**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☒ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)